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# Measurement of the degree of dispersion of pigments in water-based flexographic inks using chromatographic methods.

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# MEASUREMENT OF THE DEGREE OF DISPERSION OF PIGMENTS IN WATER-BASED FLEXOGRAPHIC INKS USING CHROMATOGRAPHIC METHODS

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## Abstract

Printing inks are often prepared by dispersion of dry, powdered pigments in a fluid vehicle. The dry, powdered pigments comprise 30-100 μm size agglomerates and aggregates of submicroscopic primary particles. These large agglomerates and aggregates are broken down to much smaller sizes by mechanical shear, e.g., by ball-milling.

The degree of dispersion of a printing ink can be measured definitively by electron microscopy or ultracentrifugation, but these methods are not easily adapted to routine industrial practice. The routine industrial methods used to measure degree os dispersion include gloss of printed ink films, sieve analysis of diluted inks, fineness-of-grind measurements using the NPIRI Production Grindometer, and tinting strength. Sieve analysis, print gloss, and fineness of grind detect only the largest particles in the dispersion, while tinting strength is at best only an indirect measure of particle size distribution. Therefore, there is a need for a definitive method of measurement that can be used in routine industrial practice.

Similar problems are encountered in other fields, e.g., polymer latexes. One approach developed recently to measure the particle size distribution of latexes is hydrodynamic chromatography. In this method, the diluted latex is pumped through a long cylindrical column packed with relatively large uniform-size non-porous spheres at rates varying with particle size, the largest appearing first and the smallest last. Detection of the particles in the effluent stream

by light scattering or refractive index gives a chromatogram, which is a measure of the latex particle size distribution. For example, a 12-foot column packed with 20 μm size styrene-divinylbenzene copolymer spheres allows measurements of latex particle size distribution over the size range 0.05-0.5 μm.

This paper describes the use of hydrodynamic chromatography as well as other chromatographic methods to determine the degree of dispersion of pigments in water-based flexographic inks. Dry, powdered pigments such as lead chromate and diarylide yellow were ball-milled into water-based grinding vehicles such as Joncryl 67. Samples were taken at different ball-milling times and analyzed by chromatographic methods, fineness-of-grind measurements, electron microscopy, and a new color strength method described in a parallel work made in this laboratory. The hydrodynamic chromatographic columns used were packed with 20 μm size spheres, which can detect particles up to 0.5 μm size, or 60 μm size spheres, which can detect particles as large as ca. 1 μm. Also, since some of the agglomerates and aggregates in samples milled for a short time were larger than 1 μm in size, a 300-foot long 20 μm-diameter capillary column was used in place of the packed-sphere column. This latter method is called tubular pinch chromatography or capillary chromatography. The results of the chromatographic measurements are described and compared with the elctron microscopic and color strength measurements, and the prognosis for development of this new method for routine industrial practice is discussed.

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Chapter 1

# The Assessment of Pigment Dispersion

## I. Introduction

Classicaly, a dispersion is composed primarily of a combination of pigment, binder, and solvent. As a physical system, the model dispersion would be a stable suspension of discrete primary pigment particles homogeneously and uniformly distributed in a liquid medium.

From measurements of nitrogen surface areas and densities, the order of magnitude of the basic particle sizes of pigments can be readily calculated from the simple formula : $S = 6 / \rho d$ where S is the nitrogen surface area, $\rho$ is the density, and d is the mean diameter of the basic particles. The calculations show that the basic particle size of most pigments is below 1 $\mu$m. With many organic pigments and most carbon blacks, the basic particle size is below 1 $\mu$m. On the other hand, in the full strength powder pigments sold commercially, the smallest speck of powder must be at least 20 $\mu$m in size; otherwise the pigments would not be a powder but would be in the form of a dust or smoke. In the commercial powder forms of pigments, therefore, the basic particles must be present in the form of closely packed aggregates, each speck of powder containing at least $10^6$ basic particles.

In use, the pigment is incorporated into a suitable vehicle and the system is ground, milled or dispersed in order to break down these aggregates as far as possible. This process takes equipment, energy and time, and requires supervision; it, therefore, costs money and there is a strong financial inducement to control the dispersion

process to avoid unnecessary cost.

As the dispersion proceeds, the technological properties of the system change. The colour strength increases, as does the brightness and gloss. These improvements are usually welcome. Less welcome may be increases in viscosity, greater deviation from Newtonian flow, and possible decreases in opacity. To get the correct combination of properties, and to ensure standardization from batch to batch, again requires control of the dispersing process.

The control of the dispersion process is therefore important, from the viewpoint of both cost and performance. Control requires measurement of the dispersion state so that the process can be stopped at any desired stage. It is the purpose of this chapter to survey actual and potential methods of assessing pigment dispersion on the basis of previous studies from W. Carr, V.T. Crowl and others (1.1, 1.2, 1.3, 1.4, 1.5, 1.6) and to comment on their suitability in order to compare them with the new method we used, which will be described later.

## II. Criteria

To help decide whether any particular technique would be suitable for pigments, W. Carr (1.3) has defined some criteria by which the technique can be judged. These criteria are readily apparent to anyone familiar with pigment technology. They are called sensitivity, versatility and applicability.

The first criterion, sensitivity, is the most important one as it is basic. It is now well established, from a variety of techniques, that in practical pigmented systems, the pigment particles are in the sub-micron size range. Accordingly, any method of size determination

will not be suitable for pigments if it cannot deal with the submicron size range.

The second criterion, versatility, stems from the wide variety of pigments and vehicles that are encountered in practice. Suitable methods for pigmented systems should therefore be capable of use with all types of vehicles, aqueous and non-aqueous, and be unaffected by the presence of solutes.

The third criterion, applicability, stems from the colloidal nature of pigment dispersions. This means that a pigmented system is an equilibrium system, representing a balance between the forces of attraction and repulsion. If the system has to be diluted for the purpose of the experiment, then there is always a possibility of dilution shock occuring which will give coarser size distributions than the original true one. If the measuring technique involves the application of shear to the system, then it is possible that the size distributions obtained will be finer than the original true one. This susceptibility of the pigmented system to the effect of external forces and alterations must always be kept in mind.

## III. Classification

Using these three criteria, we can now survey various size-measuring techniques to determine their suitability for application to pigmented systems. To ensure clarity and order, the following classification will be used : wet systems and dry systems.

The wet systems will include materials such as paints, printing inks, paper-coating mixtures, etc., before they are applied and while they are still in a fluid state. The dry systems will include

the films derived from such products, as well as mass pigmented products.

In each of these two major classifications, two sub-divisions will be used, namely indirect and direct. Indirect methods deal with the measurement of some property of the system other than particle size, which is connected in some known way with the particle size of the pigments. Direct methods deal with the actual physical measurements of the size or size distributions of the pigment particles in the system.

IV. Wet systems

1. Indirect methods

As indirect methods, we could mention the measurement of flow properties (1.7) as a means of following pigment dispersion and measuring it. It has many advantages : there is no danger of dilution shock; only small shear is applied to the system; and quick and easy measurements are made with modern instruments. But the major drawback is in the interpretation of the results, that is, in relating the flow properties of the system to the dispersion levels of the pigment in the system.

Another method for following the dispersion process would be provided by the measurements of changes in dielectric properties in the system. Again, there would be no necessity for diluting the system and no necessity to apply any form of shear to this system. But it is observed that, although dielectric changes did occur in some pigmented systems as dispersion progressed, with most pigments, the extent of the changes was so small as to make the method unsuitable and very

poor, especially in the sub-micron range.

Optical density measurements can also be used as an indirect way of determining the level of pigment dispersion, and as a technique, it has many advantages. It is fairly rapid and relatively simple. The curves of extinction coefficient versus particle size, whether determined empirically (1.8) or theoretically (1.9), have quite steep slopes in the sub-micron range. It is applicable to all types of systems, aqueous or non-aqueous, and is not affected by the presence of solutes in the liquid phase providing they are colourless. There are, however, three drawbacks : the system has to be diluted considerably; a master curve is necessary for the particular pigment; and the method only gives a mean diameter and not a size distribution.

Hindered settling is another technique that can be applied to pigmented systems and which is claimed to give information on the degree of dispersion (1.10). The concentration of pigment particles must be 1% or more, and the settling takes place under gravity, the rate of settling being measured as well as the final sediment. If the measurements are carried out on a pigment dispersed in a solvent alone and then dispersed in the solvent containing resin, information can be deduced on the basis of the dispersing power of the resin. It is believed that this technique provides a simple, inexpensive way of classifying dispersions as good or bad, but that it cannot be used for following or identifying small changes in dispersion.

2. Direct methods

Possible methods can be discussed under two headings, electronic and sedimentation. Sieving with woven wire mesh screens is possi-

bly the simplest method, but, unfortunately, its range of applicability is normally restricted to particles that are 38 $\mu$m or larger in size [1.11]. The Coulter Counter is the best known example of electronic size-measuring methods [1.12], and is based on the Coulter principle of letting the dispersion flow through a narrow aperture. There is no doubt that this instrument represents a major step forward in particle size measurement. It is simple in function and is quick and accurate. However, it is fairly generally accepted that it is not sensitive enough to deal with particles in the sub-micron range. It is also doubtful whether it could be used successfully in most commercial non-aqueous systems, because the differences in conductivity between the pigments and the media are much smaller.

A second method of size analysis can also be taken into account based on the theory and practice of free sedimentation and Stokes' law. It is applicable to all dispersed systems, whether they are aqueous or non-aqueous, and is not affected by the presence of solutes such as resins, surfactants, etc., in the continuous phase. But what is crucial is that the sedimentation must be free and unhindered, and, therefore, the original system must be diluted considerably. Gravity sedimentation is too slow to classify particles which are all in the sub-micron range. Centrifugal sedimentation can separate such particles in a reasonable time if the speed of revolution is high enough. The best known instrument based on this method is probably the Joyce-Loebl disc centrifuge [1.13,1.14,1.15]. The method has, hence, a number of weaknesses and limitations. As we have already indicated, the system has to be diluted and therefore dilution shock has to be avoided or

minimized. The method is essentially restricted, in practice, to non-bleeding organic pigments because of the analytical problems associated with inorganic pigments. Even with organic pigments, the method is slow. Normally eight to ten separate spinnings have to be carried out in order to get eight to ten different size fractions; then these fractions have to be evaporated to dryness, taken up in a solvent and their pigment content determined by analysis. All this takes time and, from start to finish, a particle size distribution curve will take about one and a half days to determine. This means that the method can only be considered as a research tool.

But many of these drawbacks can be overcome by the use of a Photosedimentometer Attachment (PSA)[1.3], which was a development designed for use with the disc centrifuge. At first, the actual experimental time is cut down dramatically because only one spinning is required, and it gives the data for a complete size distribution curve. Furthermore, no analytical step is required, which widens the scope of the method to include all pigments, whether organic, inorganic or carbon black. Extenders, and emulsions and resin dispersions can also be handled. On the other hand, because it is a sedimentometer technique, the original pigmented systems have to be diluted and this always brings on the dangers of dilution shock. Besides, because only one spinning is used, the speed at which this is carried out has to be carefully chosen, so that both coarse and fine particles in the system can be accurately sized.

If the beam of light used as the sensing mechanism in the photosedimentometer technique is replaced by a stream of X-rays, there

is little, if any, difference between the results of the X-ray sedimentation technique and the absolute method. However, the absorbing capacity of pigments for X-rays is a function of their atomic numbers, and consequently, X-ray instruments only appear to be suitable for inorganic pigments, and not for organic pigments and carbon blacks (1.16).

## V. Dry systems

### 1. Indirect methods

An interesting method of measuring dispersion in this case would be the color strength measurement. It has long been known that, as the grinding proceeds, the color strength will often increase. Color strengths can be compared very accurately by the human eye and can also be measured instrumentally by a variety of spectrophotometers (1.17,1.18). This method is straightforward and very sensitive, particularly in the regions of good dispersion. Essentially a comparative method, it can be converted into an equally sensitive absolute method if a master curve of color strength versus particle size is available. On the other hand, it must be appreciated that color strengths are only indicative of the pigment dispersion in the final dry film; some phenomena such as flooding can give erroneous values. Besides, color strength measurements do not give direct information on the particle size distribution. But, anyway, they represent an easy and accurate way of assessing pigment dispersion in the sub-micron range, especially for air-drying decorative paints and paste inks. For such systems, only one master curve is needed for absolute values, and this can readily be determined for the paints, and the oil inks

which are usually fully compatible with them.

It is also known that, as the degree of dispersion increases, the gloss of the subsequent films increases. However, it was shown that specular gloss does increase with dispersion in the coarser region but tends to level off once the mean diameter is reduced to about 0.3-0.4 $\mu$m [1.19]. Besides, gloss will also vary with time even when panels are stored in the dark [1.18].

A third method can be provided using optical density measurements, if the film thickness is known and if the film is not opaque in itself and has been prepared on a transparent substrate. These measurements can be used to determine the absolute level of dispersion if the exact relationship between extinction coefficient and particle size is known. This relationship can be determined experimentally or it can be derived from the application of the Mie theory. As in the wet state, the curves of extinction coefficient versus particle size have quite steep slopes in the sub-micron region, so that the method is sensitive, and it is applicable to all types of systems, aqueous or non-aqueous. Again, the dispersion has to be diluted drastically and the films have to be prepared on a transparent substrate. One thing which is interesting about this method is that it can be used in both the wet and dry states, and does, therefore, offer a means whereby dispersion levels in the dry films can be directly compared with the corresponding dispersion levels in the wet products from which they were derived. It can, therefore, be used to study the effects of drying mechanisms on the pigment dispersion.

2. Direct methods

If a photograph of the pigment dispersion in the dry state can be obtained, whether from a surface coating or a mass pigmented product,the size of the particles can be measured at leisure and a size distribution curve can be obtained. For particles known to be in the sub-micron region, optical microscopy is not adequate and electron microscopy is required (1.20). It is a direct method of assessing pigment dispersion scores on the grounds of sensitivity, versatility and applicability. However, the equipment is still expensive and requires a specialist operator to get the best results. It is not a rapid method, because the preparation of specimens for the electron microscope is a delicate task which cannot be hurried. Besides, to determine a size distribution, it is commonly agreed that it can only be obtained from electron micrographs when the counting and sizing is done manually in a tedious, time-consuming manner or automatically, using very expensive equipment (1.21).

VI. Conclusion and scope of the present work

These methods, however, are more often used as laboratory tests rather than as production quality control tests. This is due to one of several reasons which may include cost, time required, instrumentation, complexity and sensitivity. One of the most widely used quality control test for the degree of dispersion is the fineness of grind (1.22).

Fineness of grind gives us a direct measure of the particle size of the coarsest fraction of a dispersion. In practice, a fineness of grind would be specified for a given dispersion formula in terms

of particle size or fineness gauge reading. The dispersion would then be ground to meet this specification. But there are shortcomings of the fineness test as a quality control test for measuring degree of dispersion. The first is that many of the fine pigments used in the industry today require fineness below the resolution limits of the fineness gauge in order to develop optical properties. Secondly, the fineness gauge only measures the coarse pigment particle fraction of a dispersion and does not give us any measure of particle size distribution. As related to degree of dispersion, particle size distribution is more important than maximum particle size. Despite these shortcomings, the fineness of grind test does find its place as a quick, inexpensive and reproducible production quality control test. The reader is referred to ASTM D 1210-64, " Standard Method of Test for Fineness of Dispersion of Pigment-Vehicle Systems ", for a fuller explanation of this test. It should be noted that fineness of grind readings are designated by many different units or readings. Table 1.1 indicates the various gauge readings used in measuring fineness of grind and relates one to another, and to particle size in various units.

This paper will introduce a new method for measuring the degree of dispersion of a particular pigmented system in which we were primarily interested, i.e. water-based flexographic inks. To compare our results, we will use two direct methods; the first has just been introduced, and comprises the test for fineness of grind, using a NPIRI grind gauge which will be described later. The second will give us a more direct accurate measurement, and will require the use of the

TABLE I.1

Particle Size vs. Gauge Readings

| Particle Size | | | Gauge Readings | | |
|---|---|---|---|---|---|
| Mils | Microns | Inches | Hegman | Production Club | NPIRI[a] |
| 0.00 | 0.00 | 0.00000 | 8 | 10 | 0 |
| 0.10 | 2.54 | 0.00010 | | | 1 |
| 0.20 | 5.08 | 0.00020 | | | 2 |
| 0.25 | 6.35 | 0.00025 | 7½ | | |
| 0.30 | 7.62 | 0.00030 | | | 3 |
| 0.40 | 10.16 | 0.00040 | | 9 | 4 |
| 0.50 | 12.70 | 0.00050 | 7 | | 5 |
| 0.60 | 15.24 | 0.00060 | | | 6 |
| 0.70 | 17.78 | 0.00070 | | | 7 |
| 0.75 | 19.05 | 0.00075 | 6½ | | |
| 0.80 | 20.32 | 0.00080 | | 8 | 8 |
| 0.90 | 22.86 | 0.00090 | | | 9 |
| 1.00 | 25.40 | 0.00100 | 6 | | 10 |
| 1.20 | 30.48 | 0.00120 | | 7 | |
| 1.25 | 31.75 | 0.00125 | 5½ | | |
| 1.50 | 38.10 | 0.00150 | 5 | | |
| 1.60 | 40.64 | 0.00160 | | 6 | |
| 1.75 | 44.45 | 0.00175 | 4½ | | |
| 2.00 | 50.80 | 0.00200 | 4 | 5 | |
| 2.25 | 57.15 | 0.00225 | 3½ | | |
| 2.40 | 60.96 | 0.00240 | | 4 | |
| 2.50 | 63.50 | 0.00250 | 3 | | |
| 2.75 | 69.85 | 0.00275 | 2½ | | |
| 2.80 | 71.12 | 0.00280 | | 3 | |
| 3.00 | 76.20 | 0.00300 | 2 | | |
| 3.20 | 81.28 | 0.00320 | | 2 | |
| 3.25 | 82.55 | 0.00325 | 1½ | | |
| 3.50 | 88.90 | 0.00350 | 1 | | |
| 3.60 | 91.44 | 0.00360 | | 1 | |
| 3.75 | 95.25 | 0.00375 | ½ | | |
| 4.00 | 101.60 | 0.00400 | 0 | 0 | |

(a) National Printing Ink Research Institute.

electron microscope.

This new method is based on previous studies of the measurement of particle size and particle size distribution of synthetic polymer latexes using a system related to colloidal particle chromatography. It comprises two different types of chromatography measurement, hydrodynamic chromatography and a capillary chromatography technique. The former is especially suited for measurements in the sub-micron region and therefore could be used to measure the degree

of dispersion at the end of the dispersion process, whereas the latter, which is more reliable for the over-1 μm region, could be used to measure the degree of dispersion at the beginning.

The two following chapters describe these new kinds of measurements, beginning with an introduction to the colloidal chromatography. Then, we will describe the particular system used, namely, water-based flexographic inks, their dispersion process and the equipment used. We will then provide a brief explanation on how to prepare the different samples for the chromatographic methods, as a measure of the milling time. As a conclusion, and on the basis of the criteria described previously, we will compare this method with the others and will discuss its possible limitations.

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Chapter 2

## Introduction to Colloidal Chromatography

### I. General background

The control of particle size by means of reproducible, accurate and fairly simple analysis is of primary importance in coatings technology. Techniques such as scanning electron microscopy, light scattering, centrifugation, fractional creaming, and small X-ray scattering have been used to determine particle size distribution of colloidal dispersions, but are quite often time-consuming and unsuitable as quality control methods, and therefore limited in their specific applications.

Since the early 1960's, gel permeation chromatography (GPC) has found wide application for the determination of molecular weight distributions of polymer molecules in solution. It is one of the newest forms of liquid chromatography and has found use in both aqueous and non-aqueous systems. In GPC, a sample of solubilized polymer is injected or " shot " into a constant flowing eluant or mobile phase, which is pumped through a column packed with suitable material to get the desired separation. Fractionation in GPC occurs through a porous matrix, with the pores closely controlled in size. The molecules which are too large to enter any of the pores in the matrix pass directly down through the column in the interstitial regions between the porous particles and are eluted first from the column. Molecules of intermediate size with dimensions similar to the pores of the packing can enter some pores but not others, and will be retarded during their progression. The smallest molecules are able to

enter every pore of the matrix and will be retarded to the greatest extent, eluting last from the column. The output of the GPC chromatogram of a polydisperse sample can easily be converted into a molecular weight distribution of the polymer.

Similarly, column chromatography has found great use by colloid chemists for the analogous separation of colloidal sols. Several distinct techniques have emerged in this field. The four major areas of particle chromatography can be classified into nonporous and porous packed systems, open capillary tubular systems, and field-flow fractionation, and are summarized in Figure 2.1 . The applicable range of chromatographic and other particle size methods are presented in Figure 2.2 .

The classification of packed columns can be conveniently separated into nonporous and porous packed systems. For the purpose of this work, we will focus our attention only on the nonporous packed systems and the open capillary tubular systems.

Under nonporous packing is the technique known as hydrodynamic chromatography (HDC), originally developed by H. Small for the determination of the particle size of colloidal latexes (2.1) . In HDC, particle separation arises predominantly from an interaction between the finite particle size and mobile phase interstitial velocity profiles. In this sense, HDC shows some similarity with gel permeation chromatography but there are also several important differences. For instance, both techniques are known to produce symmetrical, bell-shaped chromatograms, as well as calibration curves which display semi-logarithmic behaviour of hydrodynamic volume versus residence

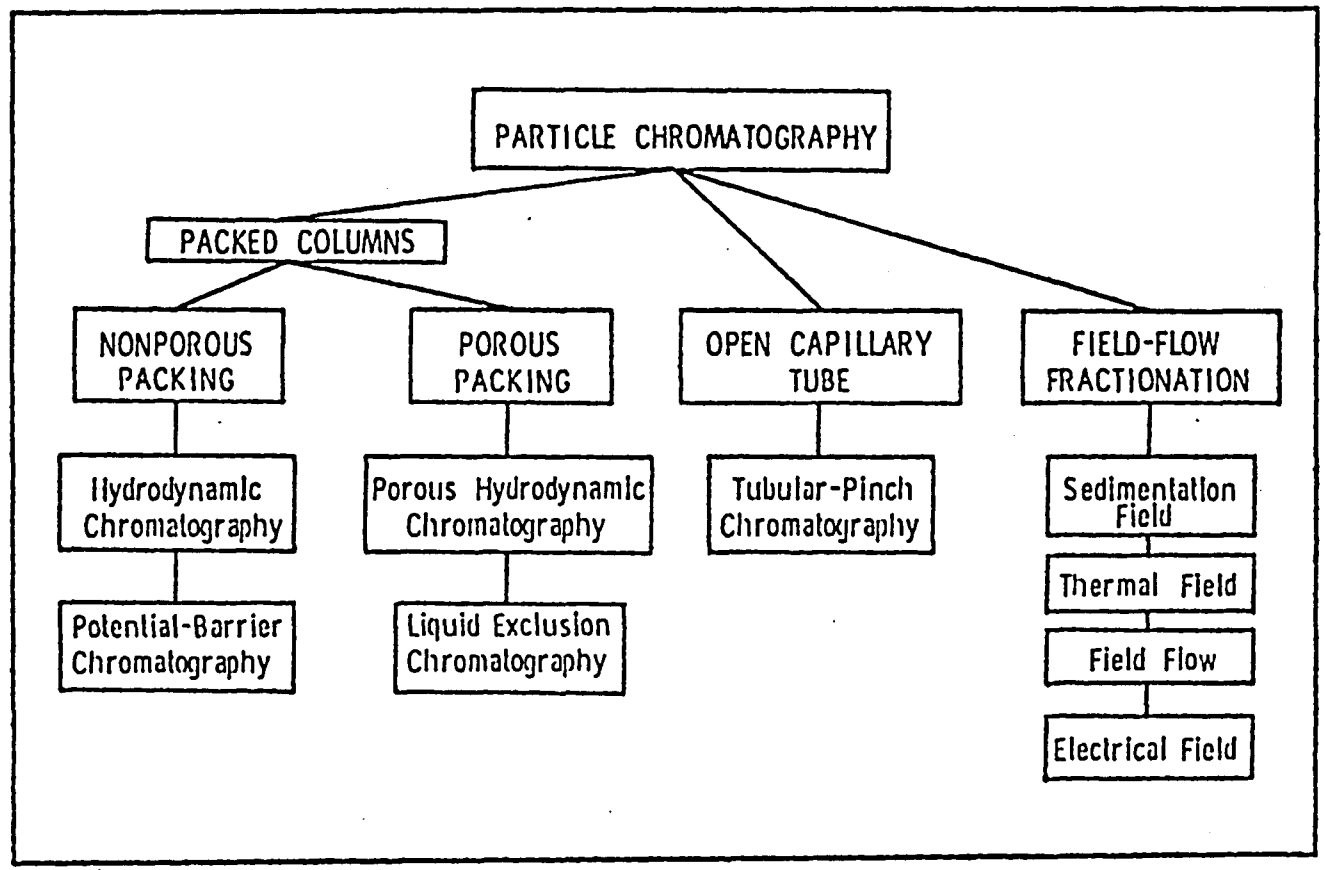


Figure 2.1 Classification of principle areas of colloidal particle chromatography.

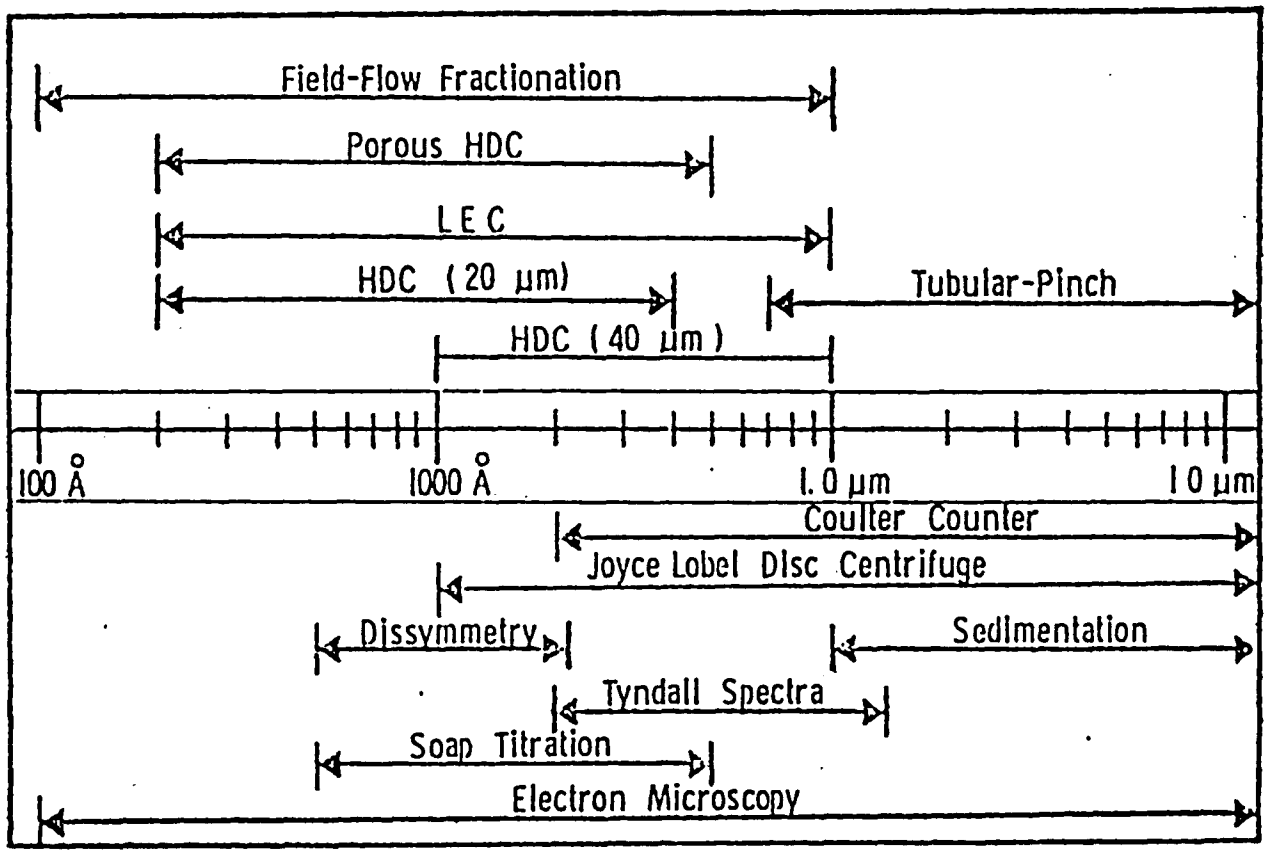


Figure 2.2 Applicable range of chromatographic and other common particle size analytical methods.

time. The major difference is that in HDC the colloidal particles are not in solution, but are suspended in the dispersed phase and the column packing is not porous but consists of uniform solid spheres. HDC is unique in that the separation forces appear to be derived exclusively from conditions operating in the interstitial volume of the bed. The separation of colloidal particles takes place under the influence of flow alone, a circumstance that was originally predicted independently by DiMarzio and Guttman [2.2,2.3] and probably first observed by Pedersen [2.4] who obtained separation of proteins by pumping them through beds packed with glass spheres of suitably small diameter. HDC can be considered as a single-phase chromatographic system.

It is best to consider the interstitial regions in the packed bed as a system of capillaries. For fluid flow within a capillary tube, it is well known that a velocity profile exists such that the velocity of the fluid is maximum at the center, decreasing as it approaches the wall. A colloidal particle injected into this laminar flow will by Brownian motion make radial excursions normal to the direction of flow, thereby sampling and adopting velocities across the capillary. The center of the particle due to its finite size will be excluded from the slowest streamlines closest to the capillary wall. Thus, a particle will travel with an average velocity greater than that of the mobile phase fluid, with the velocity increasing with increasing ratio of particle size to capillary radius. This results in the normal elution order of samples observed in HDC : first large particles, followed by small particles, followed by the mobile phase

eluant or any dissolved molecular species present in the eluant. The separation of colloidal particles in HDC is independent of the chemical composition of the packing since the elution of particles can be attributed to flow alone. The potential to use HDC for size analysis is due to its speed, ease of analysis and good reproducibility, but it can only be applied to systems within the sub-micron range.

Particle separation by flow through open-capillary tubes has been called tubular-pinch chromatography. Here behavior similar to HDC --largest particles eluting first followed by particles of decreasing dimensions, and all particles ahead of the liquid with which they started-- is exhibited by particles when injected at the head of a long, open-capillary tube and caused to pass through the tube by the flow of more liquid. Recent investigations have shown this to be a promising method for the fractionation of particles greater than one micron in diameter [2.5,2.6,2.7].

Radial displacement of particles flowing inside tubes has been known for many years. Quantitative evaluation began with the study of Segre and Silberberg [2.8,2.9], who found a suspension of neutrally buoyant spherical particles flowing through a constant-diameter capillary of circular cross section become inhomogeneous, with the particles concentrated in an annular ring about the tube center. This equilibrium position for the particles was found to be approximately 0.6 of the tube radius measured from the axis and independent of the initial particle lateral position. The phenomenon was called the " tubular pinch effect ", and this method is often referred to as tubular pinch chromatography. In contrast to HDC where the separation involves

Brownian motion of sub-micron particles, this method shows increased resolution for particles greater than one micron due to the non-Brownian tubular pinch effect.

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Chapter 3

## Description and Theoretical Background of the New Chromatographic Methods for Assessing Pigment Dispersion

### I. The nonporous particle chromatography : HDC

#### 1. Introduction

The application of chromatographic techniques for the determination of particle sizes of colloidal latexes was realized when H. Small [2.1,3.1,3.2] presented detailed experimental evidence for HDC using columns packed with nonporous beads. The separation process in HDC is derived exclusively from forces arising during flow through the interstitial regions between the packing beads.

Small's original work on HDC included only a qualitative analysis for the separation mechanism and was based on calculations by DiMarzio and Guttman [2.2,2.3] for the separation of polymer molecules in capillary tubes. Recently, Stoisits et al. [3.3], McHugh et al. [3.4], Silebi [3.5], and Nagy [3.6] have demonstrated that the separation in HDC can be quantitatively founded using an equivalent capillary model in which the flow separation is based on calculations for the convected Brownian motion of colloidal particles in a capillary tube in the presence of an electrostatic force field. Prieve and Hoysan have also reported similar calculations [3.7]. Buffham recently investigated model independent aspects of HDC in relating the speed of chromatographic transients to equilibrium properties [3.8] in a similar manner to that originally done by Silebi and McHugh [3.5]. This model enables calculation of the column separation factor, $R_F$, in terms of relevant experimental parameters, such as the ionic strength of the mobile

phase. A particle size distribution (PSD) of polydisperse samples can also be computed from experimental HDC chromatograms (3.9,3.10,3.11,3.6).

Let us mention here that it is not necessarily the purpose of this work to be quantitative. A pigmented system is much more complex than even a polydisperse polymer latex, and since such systems have not yet been studied by HDC method, it is our main goal to determine whether this new method can be used to assess pigment dispersion. However, in order to compare it with what was already described in the litterature, and referred to in Chapter 1, we need a certain understanding of the basic behavior of the HDC as well as how to apply it in our own case, on the basis of the previous works carried out for colloidal polymer latexes.

2. Apparatus

A flow diagram for the HDC apparatus is shown in Figure 3.1 . This instrument comprises a solvent delivering pump, pressure gauge, pressure relief safety valve, pre-column, if needed, sample injection valve, separation column(s), variable wavelength ultraviolet-visible detector, and strip-chart recorder.

a. The eluant

The eluant consists of double distilled water, surfactant, or added electrolyte,which is pumped at a constant flow rate through the system. The typical surfactant used, in our case, is the sodium lauryl sulfate from the Onyx Chemical Company ( Tradename - Maprofix S63 99% ). The chemical formula of this emulsifier is as follows : $C_{12}H_{25}SO_4Na$ SLS (MW = 288). Depending upon the ionic strength desired for the mobile phase, the concentration of the surfactant may

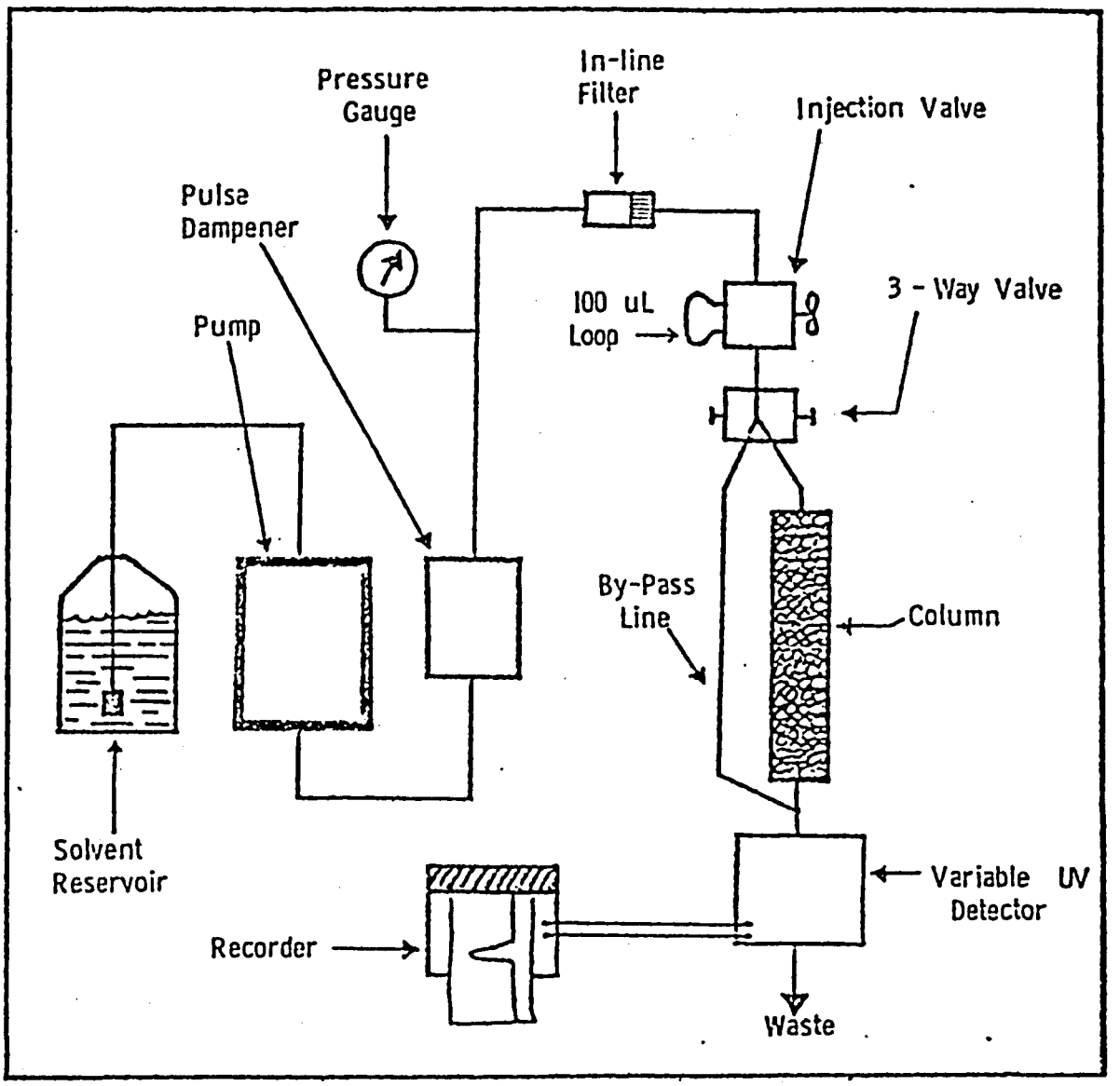


Figure 3.1 HDC experimental apparatus.

range from several millimolar to as high as 0.1 molar. To prevent bacterial formation in the eluting solution and damage of the packing material, 5.0 ml of a 37% formaldehyde solution (Fisher Scientific) is added to each liter of solution. The eluting solution is pre-filtered through a 1.0 $\mu$m Millipore membrane filter with the use of an aspirator.

b. The pumping system

The pump is either a Milton Roy Mini-Pump with a capacity of 2.7 ml/min at 1000 psi or a Laboratory Data Control Duplex Pump with a pulse dampening apparatus, with a maximum capacity of 10 ml/min at 5000 psi, The normal pressure drop of the HDC columns is approximately 450 psi at a flow rate of about 0.5 ml/min. The inlet line of the pump is connected to the mobile phase reservoir which contains a 15 $\mu$m stainless steel filter (Swagelok, # SS-2FE-15) to prevent any particulate matter from being drawn into the pump. The outlet line of the pump is connected to the safety relief valve (set for 500 psi), the pressure gauge, and then the pre-column.

c. The pre-column (optional)

The pre-column serves to dampen any remaining pulsing flow of the fluid and filter out any contaminants. The column is about 30 cm long and identical in nature to the larger three separation columns, described below.

d. The sample preparation and injection

A Chromatromix Multiport Injection valve (# R60SVK) located at the head of the first column permits injection of the sample into the system without interrupting the flow of the eluant. The volume of the

injection loop is approximately 0.08 ml. Normally one or two ml of sample is necessary to flush out the loop before filling for injection.

The samples prepared for injection into the column are normally 0.005-0.01% by weight, prepared in the eluting solution. The problems we encountered in the preparation of our pigmented samples will be described later. Usually all latex samples are pre-filtered through a 0.4 μm Millipore membrane filter prior to use, and ultrasonicated for approximately 10 seconds. Again, difficulties arose when we tried to filter out the large particles of the polydisperse pigmented systems. Most of the bigger particles tended to clog the filter, and almost all the pigment particles were retained. The same occurred with larger pore size membranes or filters, even with 5 μm filters. Consequently, the samples were injected directly.

A marker sample, or internal standard, prepared in the eluting solution is also injected during the course of a run when performing particle size analysis. The marker is a 0.0125% solution of sodium dichromate, $Na_2Cr_2O_7$.

Elution times for the different samples through the three columns are normally two hours at a flow rate of 0.5 ml/min. However, samples may be injected consecutively every 15-20 minutes. If we use only one column, at the same flow rate, and depending on the size of the packing material we use, the elution time is considerably reduced.

e. <u>The columns and the packing</u>

The three glass columns and pre-column are from Laboratory Data Control (# LC-9MA-43). The three separation columns are each 9 mm I.D. x 110 cm in length, packed with spherical styrene-divinylbenzene

copolymer beads with a nominal diameter of 20 μm. During this work, a column containing beads with an average diameter of 60 μm have also been used, in order to extend the range of the method.

The inlet and outlet parts are comprised of Teflon fitted plungers with filtering screens of 40 μm size. A small 2 to 3 mm layer of Dowex 50 resin (75-100 μm) is added on top of each screen so as to prevent packing material from being pumped through the screen. Frequent replacement of inlet screens is necessary to prevent column clogging. The columns are slurry-packed, and the packing is allowed to settle by gravity. The three columns used at first were connected in series, with the flow always being maintained in the same direction through the columns. Details of column packing and cleaning are given in the Appendix.

f. Detector

The effluent from the separation columns enters the flow cell (path length of 10mm) of the variable UV-visible detector (Laboratory Data Control, Model 1202, 200-700 nm range), where its turbidity is measured to detect the latex particles. The reference cell is normally filled and capped with a small injection of the eluting solution. Sometimes after very heavy use, the cells of the detector require cleaning, which may be easily done with a dichromate cleaning solution. The output of the detector is monitored at a range of 10 mV on a strip-chart recorder (Sargent model SR or Linear Instruments, Model 385).

g. Solvent by-pass line

In order to calculate percent recoveries of our samples, latex

or ink samples, through the HDC system, the solvent by-pass line is used, connected from the injection valve directly to the inlet part of the detector. By a comparison of relative peak areas of a sample which has passed through the by-pass line and the column, a material balance is calculated.

h. Latex standards

The latexes used for calibration purposes are monodisperse standards manufactured by the Dow Chemical Company, Midland, Michigan. The average particle diameter and standard deviation of these latexes, characterized by electron microscopy, are given in Table 3.1 . The 380 Å latex (# 47641) is a carboxylated polystyrene latex, while the others are Dow monodisperse polystyrene latexes prepared with a sulfonate emulsifier.

Table 3.1

Monodisperse Polystyrene Latexes

| Latex Code Number | Diameter (Å) | Std. Deviation (Å) | % Std. Dev. |
|---|---|---|---|
| 47641 | 380 | 75 | 19.7 |
| LS-040-A | 880 | 80 | 9.1 |
| LS-1132-B | 910 | 58 | 6.4 |
| LS-1044-E | 1090 | 27 | 2.5 |
| LS-1045-E | 1760 | 23 | 1.3 |
| LS-1047-E | 2340 | 26 | 1.1 |
| LS-1010-E | 3570 | 56 | 1.6 |

To calibrate the column packed with 60 $\mu$m size beads, it is advisable to use a few more latexes whose average particle diameters

range from 0.4 to about 1.0 μm, especially the 4000, 4400, 7940 and 11,000 Å diameter monodisperse polystyrene standard latexes.

The latex particles and marker elute through the HDC system and pass through the photometric cell which monitors the optical density versus time on the recorder. Over a range of ionic strengths the particles elute from the column with a residence time less than that of the marker species, with the residence time of the particles decreasing with increasing particle diameter serving as the basis for the separation, as shown in Figure 3.2 .

3. Review of Small's work

The rate of transport of a colloid through a packed bed can be expressed as a relative quantity $R_F$ where (2.1) :

$$R_F = \frac{\text{Rate of transport of colloid through the bed}}{\text{Rate of transport of the eluant through the bed}} \quad (3.1)$$

The transport time of the eluants through the interstitial volume of the columns is measured by observing the elution time of a suitable marker species. To be an acceptable marker, a species should have the same average velocity as that of the eluting fluid and be confined to the void space when passing through the bed. These restrictions require the marker to be of molecular size and to have no physical or chemical interaction with the packing. An ionic species such as sodium dichromate was found to be a suitable marker (2.1) . Donnan exclusion forces (3.12) prevent significant penetration of the packing by the electrolyte used as a marker. Small (2.1) noted a dependence of the elution times of an ionic marker on the eluant ionic

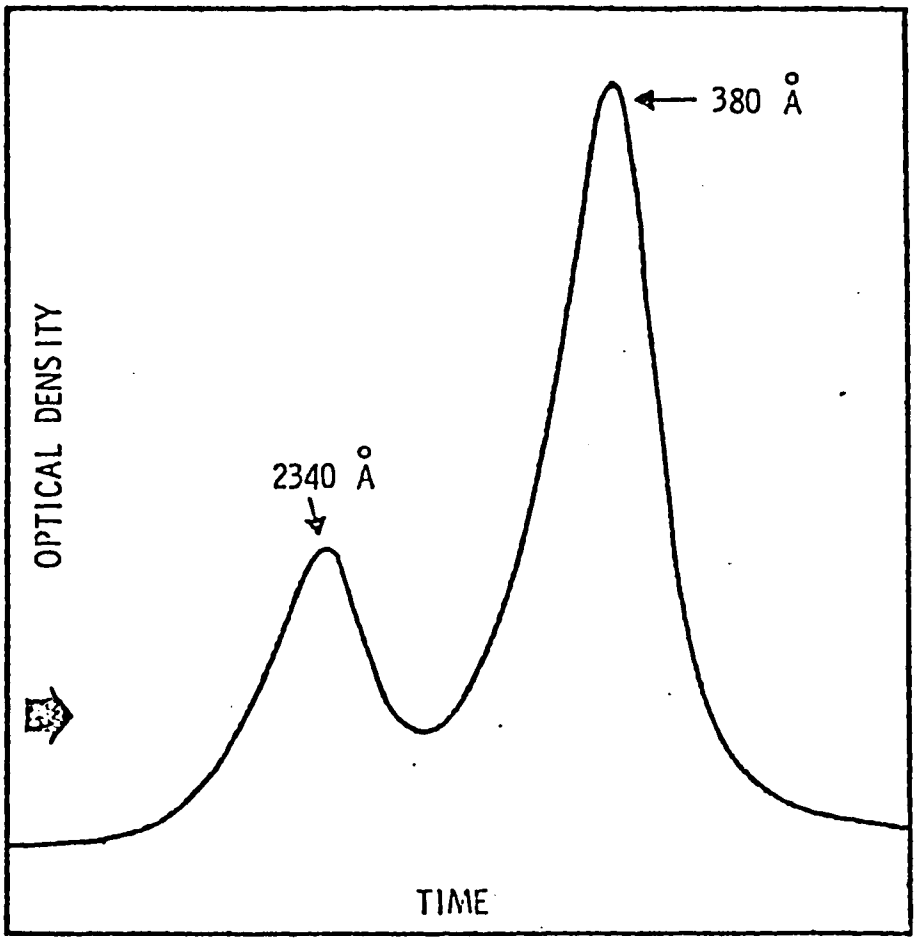


Figure 3.2 HDC separation of a mixture of 380 Å and 2340 Å polystyrene latexes.

strength which he attributed to the exclusion of the ionic marker from the ionic double layer surrounding the packing particles. He concluded that, although in most cases the markers are not a precise measure of the rate of eluant flow, this deviation does not affect the conclusions drawn from the value of $R_F$.

Small's experimental results (2.1) indicated that $R_F$ was a function of the diameters of the colloid particles and the spherical packing. The effect of variation of packing diameter on the rate of transport of monodisperse polystyrene latex particles through ion exchange beds is illustrated in Figure 3.3 . From these results, Small concluded the following :

a. $R_F$ increases with increasing particle diameter of the latex, which is the basis for the size separation.

b. As the particle size of the packing is reduced, $R_F$ increases and the slope of the $R_F$ versus diameter plot also increases; this results in improved separation of different size particles.

c. $R_F$ is always greater than unity or in other words the latex particles move more rapidly through the bed than either the carrier fluid or the low-molecular-weight soluble species.

d. Small also noted that $R_F$ is dependent on the ionic strength of the eluant (Figure 3.4). He varied the ionic strength in the eluant by increasing the amounts of sodium chloride and sodium phosphate, in addition to the sodium lauryl sulfate used to stabilize the latex. In all cases, $R_F$ increased with decreasing ionic strength.

The ionic strength effect is understandable if one considers the electrostatic interaction between the colloid and the surface of

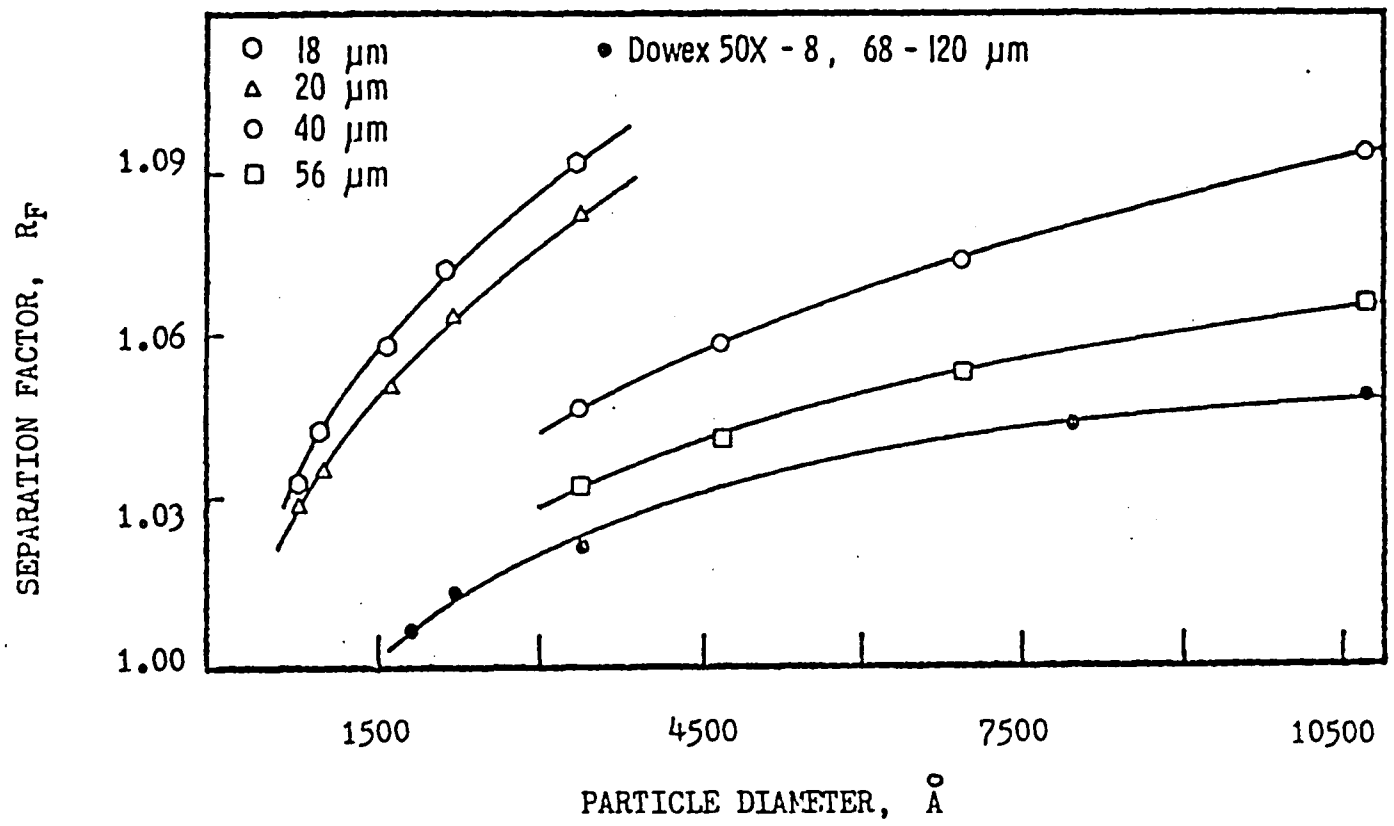


Figure 3.3 Dependence of the separation factor, $R_F$, on latex particle diameter, Rp, and packing diameter, $D_{PK}$. Data of H. Small (2.1) and also of Dowex 50WX-8 cation-exchange resin.

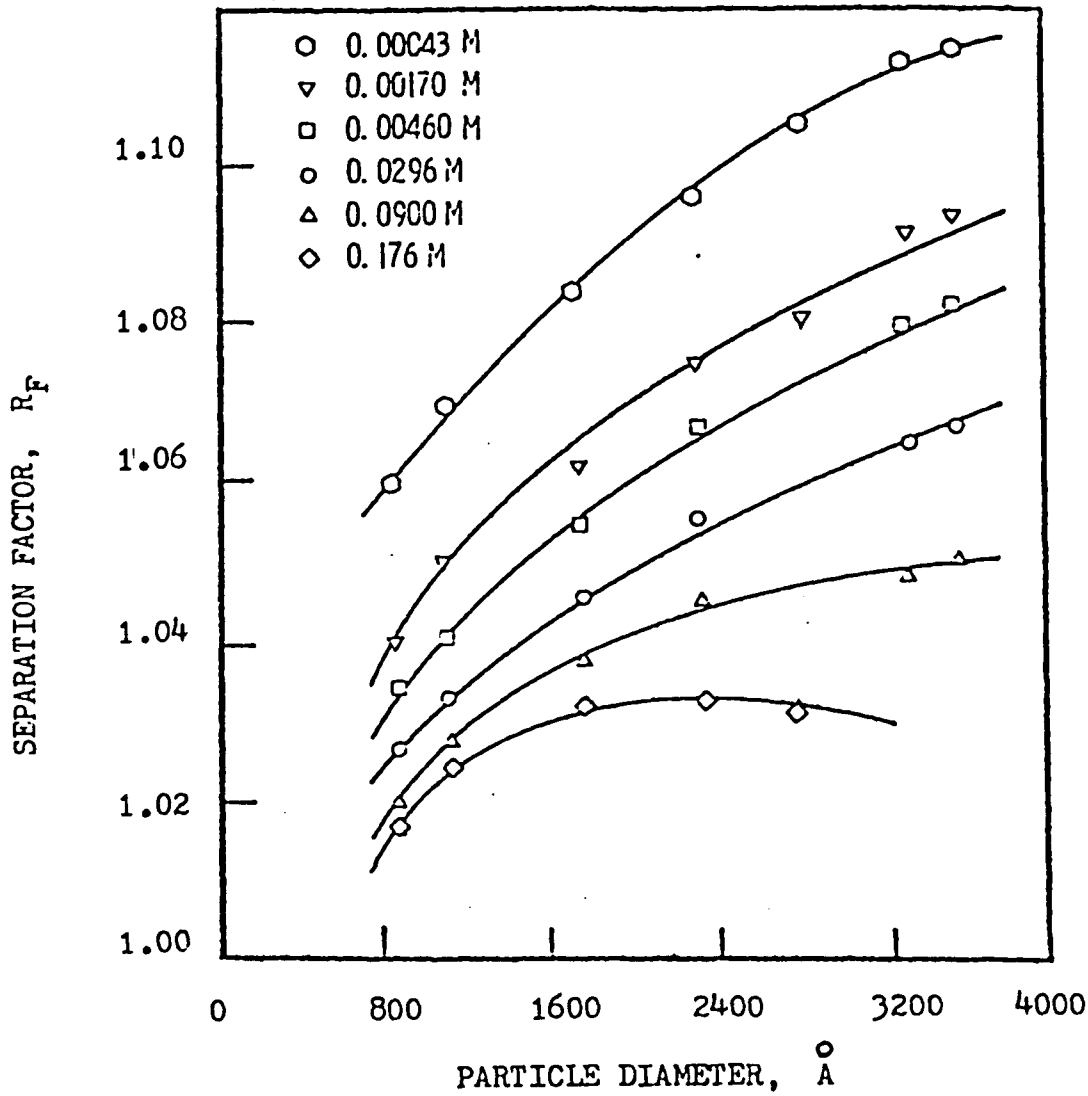


Figure 3.4 Effect of ionic strength of eluant on the separation factor, $R_F$, for polystyrene latexes. Data taken from H. Small (2.1).

the packing, both of which have associated electrical double layers. The resulting electrostatic repulsion between the colloid and the packing will determine how closely the former can approach the latter and in accordance with accepted theories of double layer interaction (3.13,3.14)

this distance at closest approach should increase with decreasing eluant ionic strength. At low ionic strength, the colloid particle will be repelled and be forced to travel in the faster moving fluid with a resulting increase in $R_F$. At higher eluant ionic concentrations, as in the two lowest curves of Figure 3.4, Small noted that some of the larger latex particles did not appear in the effluent. He attributed these effects, to a weak reversible interaction between the latex particles and the packing. At these higher ionic concentrations, the ionic double layers surrounding the latex particles and the packing are diminished, and as a result, a weak flocculation may occur. The attractive forces between the larger particles and the packing are great enough so that the particles adhere to the packing, while the smaller particles are retarded resulting in a decrease in $R_F$.

4. Material balance calculation

As stated earlier a practical upper limit for the fractionation of particle sizes exists for the HDC using 20 $\mu$m or 60 $\mu$m size packing. A material balance to determine the amount of injected sample which is recovered can be made from the resulting chromatogram by a comparison of its peak area to that for the same sample run through the column by-pass line. The peak area, Ap, can be calculated by

$$Ap = \left( \frac{O.D.}{100} \right) \frac{Q_F \, d \, n}{s} \qquad (3.8)$$

where O.D. is the optical density, $Q_F$ the flow rate, n the number of squares of the chart paper under the chromatographic peak, s the chart speed, and d the length of a square. In this manner, to calculate percent recoveries of a sample, particle size or sample concentration need not be known.

5. Calibration

Calibration of the HDC apparatus is carried out by measuring the difference in elution volume ( $\Delta V$ ) between the marker and particle peaks for several monodisperse latexes. A plot of $\Delta V$ versus log Dp (diameter of the particles) reveals a linear relationship between these quantities, an observation which has a parallel in the Gel Permeation Chromatography behavior of polymer solutions. A calibration plot using monodisperse polystyrene, poly(vinyl chloride), and poly(styrene-co-butadiene) latexes at an eluant ionic strength of 0.0013 M SLS is seen in Figure 3.5 . First, over the range of particle diameters from 880 to 3570 Å the plot is essentially linear, deviating somewhat for the smallest particle size (380 Å). Second, the calibration appears to be independent of the composition of the particle used. Finally, the whole spectrum of particle sizes between 380 and 3570 Å is encompassed within a $\Delta V$ of about 4.0 ml, or about 6% of the total column void volume. In Figure 3.6, we show the independence of eluant flow rate on the HDC calibration curves using polystyrene latexes (3.5) .

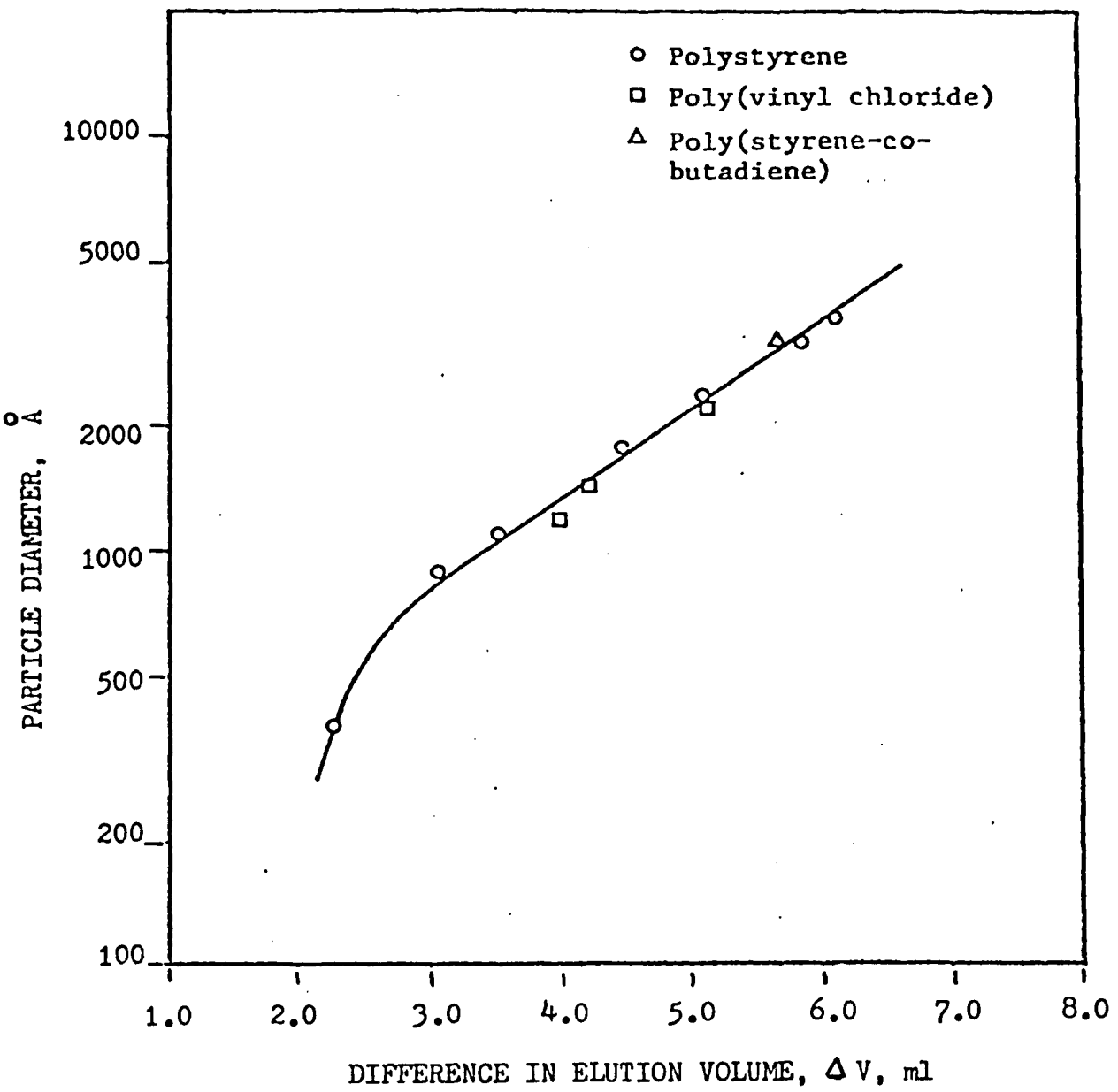


Figure 3.5 HDC calibration curve using polystyrene, poly(vinyl chloride), and poly(styrene-co-butadiene) monodisperse standards. Eluant ionic strength is 0.00129 M Acrosol MA.

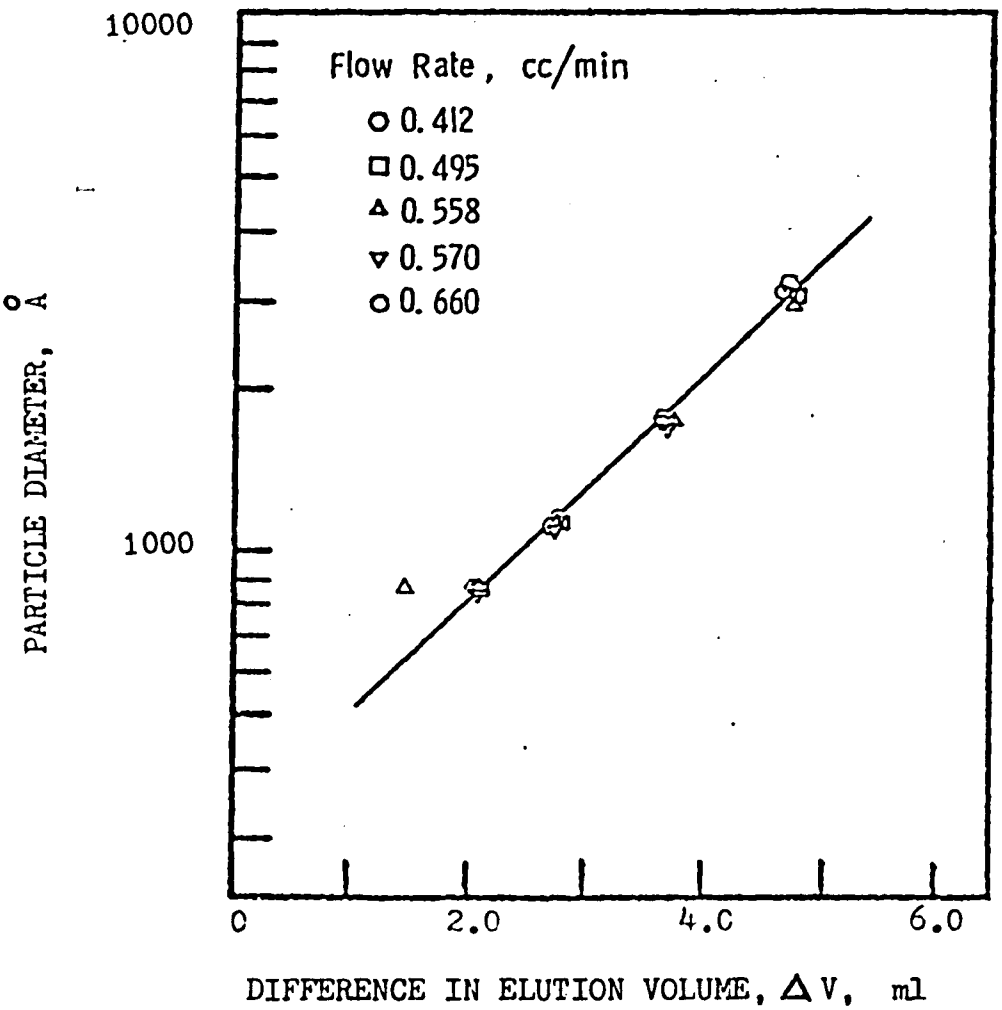


Figure 3.6 Effect of the flow rate upon the calibration curve for HDC. Eluant concentration : 0.0025 M Acrosol MA + 0.0015 M $NaHPO_4$.

In the next chapter, we will present our personal results and will show that, depending on the average diameter of the packing beads used, we can get some slight differences in the calibration curves.

6. Mechanism of separation by flow

An HDC model has been formulated (3.3,3.6) which is based on considering the interstitial spaces in the packed bed to be equivalent to a system of capillaries. When a viscous velocity profile exists such that the velocity of the fluid is maximum at the center and zero at the wall. A rigid colloidal particle injected into the capillary will make radial excursions due to Brownian motion, thereby adopting a range of velocities. The average velocity of the particle at any given time will be approximately equal to the velocity of the fluid at the center of the particle. Since the particle is rigid and has a finite size, it will be excluded from the slowest streamlines closest to the capillary wall. Therefore, the particle will have an average velocity which is greater than the mean velocity of the eluting fluid.

This difference in velocity will increase with increasing ratio of particle size to capillary radius because larger-diameter particles will be excluded from more of the slow streamlines near the capillary wall than the smaller-diameter particles. If particles of two different sizes are introduced simultaneously at the top of a capillary, the average distance between these particles will increase linearly with time as they flow through the capillary since they will have different average velocities. On the other hand, the peak widths of the distribution of particle distances about their mean value for each particle size increases as the square root of the time the

particles reside in the capillary. Therefore, by using columns with long residence time, the separation between peaks can be made large compared to the width of the peak and the particles will separate into two groups.

## II. The capillary hydrodynamic chromatography

### 1. Introduction

Transport of an aqueous suspension of particles through tubes has been examined by a number of investigators. They have generally observed that when rigid spheres are transported in a Poiseuille flow through a straight, cylindrical tube they undergo radial displacement and move along trajectories which asymptotically approach straight lines parallel to the tube axis at a fixed distance between the latter and the wall. Perhaps the first observation of the segregation of particles in a capillary was when Poiseuille [3.15] noticed that there were areas free of red cells near the walls of capillaries in the circulatory system. Taylor [3.16] later confirmed this phenomenon and also observed a particle-free region at the center of tubes in which particles are being transported by flowing fluid.

A detailed experimental analysis of particle segregation in laminar flow systems was undertaken by Segre and Silberberg [2.8, 2.9, 3.17] in the early 1960's. As a result of these studies they proposed the term " tubular pinch " to describe this focusing of particles into an annular ring. Figure 3.7 illustrates the profile of the laminar flow and the annular rings produced. They showed that a neutrally bouyant sphere being transported through a tube by Poiseuille flow is subject to radial forces that carry it to an equilibrium position

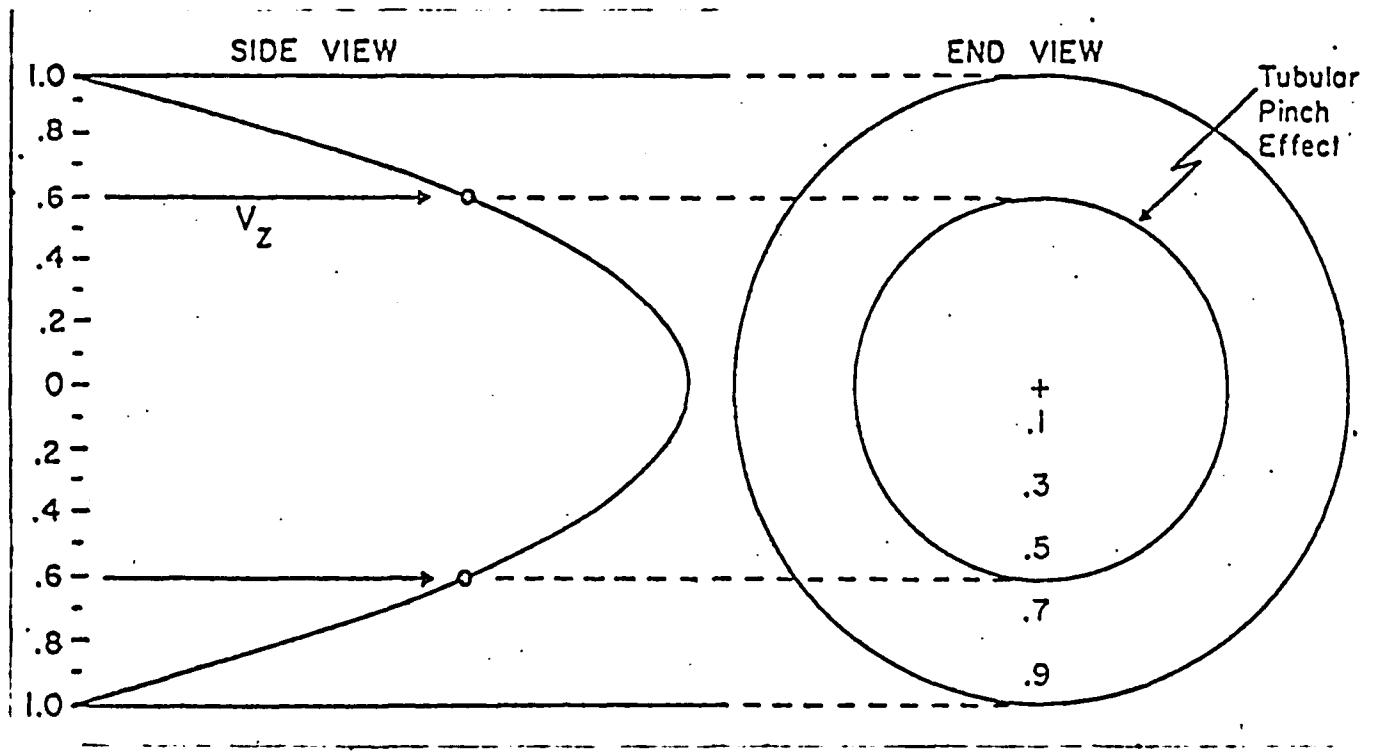


Figure 3.7 Profile of laminar flow and the annular ring produced.

at approximately 0.6 tube radii from the tube. The origin of the force causing this radial displacement or focusing is in the inertia of the moving liquid.

Examination of literature concerning the " tubular pinch effect " suggests that the radial equilibrium position of a particle in Poiseuille flow is a function of both mobile phase velocity and the ratio (a/R), where a is particle radius and R is the tube radius (3.18). By combining the data of several other groups, Walz and Grün (3.18) were able to show that particles assume equilibrium positions nearer to the tube wall when the liquid velocity is increased in a tube.

The velocity of a radially segregated particle will be the same as the liquid velovity at that position (Figure 3.7). This velocity may be obtained from the equation :

$$v_z = \frac{(P_o - P)\, R^2}{4\, \eta\, L} \left[ 1 - \left( \frac{r}{R} \right)^2 \right]$$

where $v_z$ is the liquid velocity at a given radial position, $(P_o - P)$ is the pressure drop across the column, R is the tube radius, r is the radial position, $\eta$ is the liquid viscosity, and L is tube length. A relationship, besides, can be shown between the particle diameter, $d_p$, and the radial position, r :

$$\frac{r}{R} = \left[ 1 - \frac{0.267 \quad L^2}{(P_o - P)\, R^2\, (9.64 - \log d_p)} \right]^{\frac{1}{2}}$$

This last equation predicts that small particles are also located at a radial position between 0.6 and 0.7 and that large particles focus

in an annulus near the tube axis as indicated in Figure 3.7. These theoretical values agree very well with those experimentally determined by Segre and Silberberg [3,17] in their macroparticulate studies. Although there is insufficient evidence to conclude that particle resolution in capillary hydrodynamic chromatography is the result of the " tubular pinch effect ", it is at least implied.

2. Apparatus and procedure for calibration

A reservoir containing 0.001 M sodium lauryl sulfate solution is pumped continuously through a stainless steel coiled capillary tube approximately 680 feet (207 m) long and 0.01 inches (0.254 mm) in inside diameter. The pump with a capacity of 5000 psi produced a maximum flow rate of slightly more than 1.1 ml/min through the tube. The flow rate was determined by timing the collection of the liquid exiting the system.

Monodisperse latex samples were injected through an injection valve just before entrance into the tube. The exiting samples were detected by an ultraviolet light detector with a wavelength of 254 nm and the turbidity was plotted as a function of time on a plotter unit [2.7,3.19]. The samples of known particle size (Table 3.2) were prepared in the eluting solution in concentrations ranging from 0.01 to 0.05 percent solids. To ensure that the samples were pure and monodisperse, they were first filtered, and then ultra-sonified to break up aggregates.

Samples were injected at four different flow rates to obtain a set of calibration curves for capillary chromatography (Figure 3.8). In the next chapter, we shall compare these calibration curves with

Table 3.2

| Type of particle | Particle size (Å) |
|---|---|
| Polystyrene | 380 |
| Polystyrene | 880 |
| Polystyrene | 1760 |
| Polystyrene | 2340 |
| Polystyrene | 3570 |
| Polystyrene | 7940 |
| Polystyrene | 11,000 (1.1 μm) |
| Polyvinyltoluene | 20,200 (2.02 μm) |
| Styrene-divinylbenzene copolymer | 40,000-70,000 (4-7 μm) |

the experimental results for pigment dispersion. A sodium dichromate marker was used at each flow rate to compare elution volumes; this marker elutes at the same time as the average eluting solution. (2.7,3.19)

3. Discussion of these calibration curves

The difference in elution volumes of the marker and particles is plotted versus the logarithm of particle size (Figure 3.8). The elution volume differences are shown to decrease with decreasing particle size. This corresponds to an increase in elution volume with decreasing particle size. Above 7940 Å, the elution volumes are quite reproducible, in accordance with the tubular pinch theory. Below 7940 Å, a sharp break appears in the calibration curve. For particles in the 380-3570 range, the results have a certain standard deviation, indicating that these particles are no longer in the tubular pinch regime of flow. These results agree with those of Orr et al. (2.6),

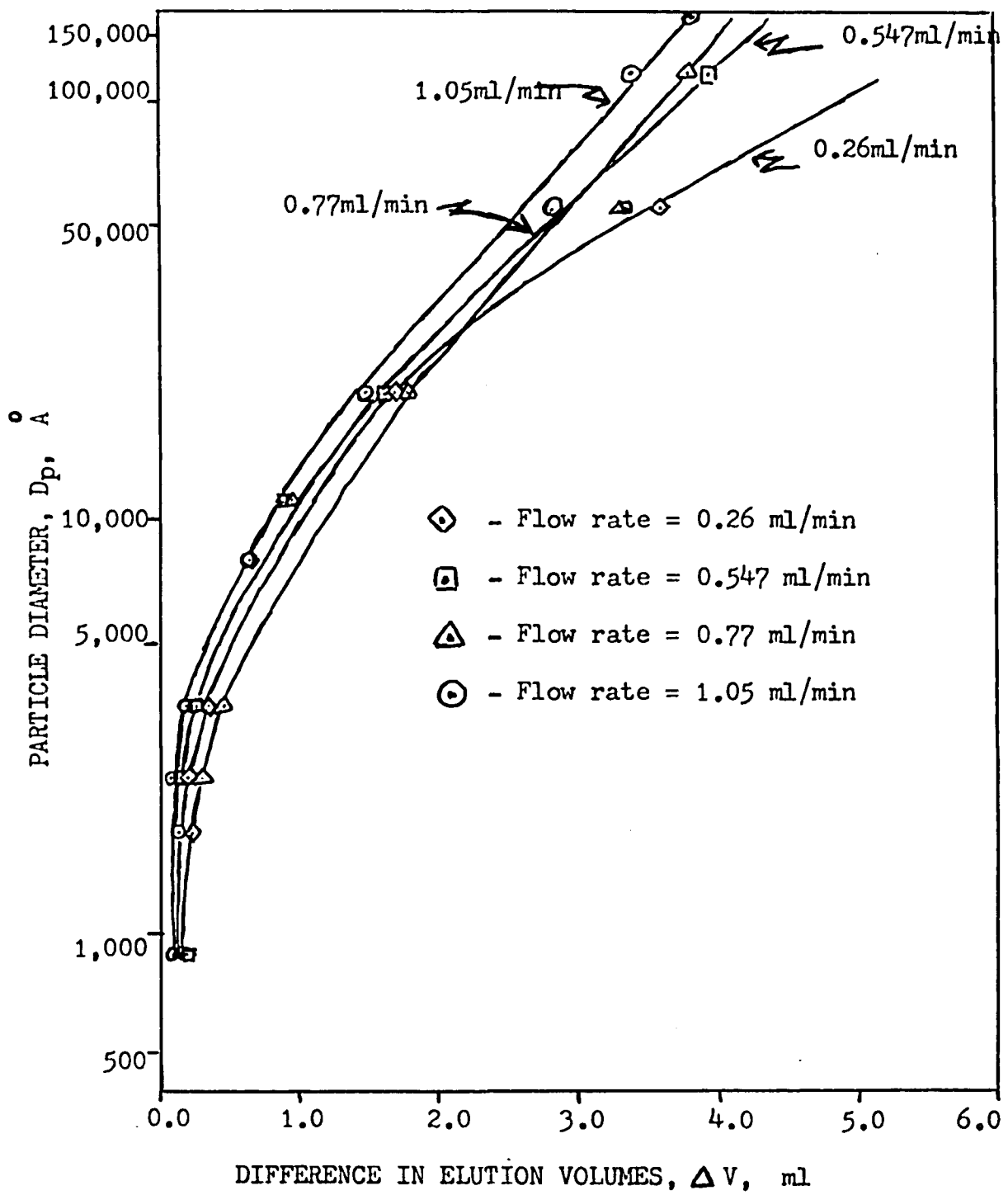


Figure 3.8 Calibration curves for capillary chromatography as a function of flow rate.

although their results indicate that the break point occurs closer to 1 $\mu$m. The reason for such a break or bend in the curve is that the smaller particles are being retained by a stagnant liquid layer at the tube wall. This retention time is not constant for a given particle size; therefore, the elution volumes will vary greatly. This is opposed to the larger particles, which attain an equilibrium position in the tube and proceed through the tube in a velocity streamline. Therefore, the reproducibility of results is good.

The resolution of the system :

$$R = \frac{(V_{R,p2} - V_{R,p_1})}{\frac{1}{2}(W_1 + W_2)}$$

where $V_{R,p_1}$ and $V_{R,P2}$ are the elution volumes of particle populations one and two, respectively, and $W_1$ and $W_2$ are the baseline peak widths of populations one and two, respectively. Thus, R is the number of average arithmetic peak widths between two neighboring peak maxima. The calculation of this resolution is shown in Table 3.3 (3.19). From this, it can be seen that for both 1 mM and 5 mM SLS eluting solution runs, the greatest resolution of particles occurs when the difference between their diameters is the greatest. Poor resolution is obtained for similar-sized particles; however, although the resolution is poor, the sizing is still accurate because of the characteristic elution volume.

The wavelength of UV light was also varied (3.19) to see the effect on resolution. For both the 1 mM and 5 mM concentrations, the resolution increased when the wavelength was increased to 260 nm, and decreased at a wavelength of 300 nm. Mullins and Orr (2.6)

Table 3.3

Resolution of the system

| Sample | $\bar{W}$ ($cm^3$) | $\bar{V}$ ($cm^3$) | Resolutions Latex 1/ Latex 2 | | | | |
|---|---|---|---|---|---|---|---|
| | | | 7940/1.1 (Å) (μm) | 7940/2.02 (Å) (μm) | 7940/4-7 (Å) (μm) | 1.1/2.02 (μm) (μm) | 1.1/4-7 (μm) (μm) |
| 1 mM SLS | | | | | | | |
| λ = 220 nm | | | | | | | |
| 7940Å | 5.55 | 13.07 | | | | | |
| 1.1 μm | 4.55 | 12.72 | | | | | |
| 2.02 μm | 3.90 | 11.85 | 0.07 | 0.26 | 0.94 | 0.21 | 0.99 |
| 4-7 μm | 0.80 | 10.05 | | | | | |
| λ = 260 nm | | | | | | | |
| 7940Å | 5.40 | 13.12 | | | | | |
| 1.1 μm | 4.31 | 12.65 | | | | | |
| 2.02 μm | 3.69 | 11.80 | 0.09 | 0.29 | 1.02 | 0.22 | 1.05 |
| 4-7 μm | 0.70 | 10.01 | | | | | |
| λ = 300 nm | | | | | | | |
| 7940Å | 5.49 | 13.16 | | | | | |
| 1.1 μm | 4.44 | 12.80 | | | | | |
| 2.02 μm | 3.84 | 11.86 | 0.07 | 0.27 | 0.97 | 0.22 | 1.02 |
| 4-7 μm | 0.70 | 10.12 | | | | | |

Table 3.3 (cont'd)

Resolution of the system

| Sample | $\bar{W}$ ($cm^3$) | $\bar{V}$ ($cm^3$) | Resolutions 7940/1.1 (Å) (μm) | 7940/2.02 (Å) (μm) | 7940/4-7 (Å) (μm) | Latex 1/ Latex 2 1.1/2.02 (μm) (μm) | 1.1/4-7 (μm) (μm) |
|---|---|---|---|---|---|---|---|
| 5 mM SLS | | | | | | | |
| $\lambda$ = 220 nm | | | | | | | |
| 7940Å | 5.23 | 13.14 | | | | | |
| 1.1 μm | 3.86 | 12.86 | | | | | |
| 2.02 μm | 2.90 | 12.20 | 0.06 | 0.23 | 0.95 | 0.19 | 1.11 |
| 4-7 μm | 0.71 | 10.21 | | | | | |
| $\lambda$ = 260 nm | | | | | | | |
| 7940Å | 5.10 | 13.28 | | | | | |
| 1.1 μm | 3.79 | 12.91 | | | | | |
| 2.02 μm | 2.90 | 12.20 | 0.08 | 0.27 | 1.04 | 0.27 | 1.18. |
| 4-7 μm | 0.84 | 10.20 | | | | | |
| $\lambda$ = 300 nm | | | | | | | |
| 7940Å | 5.25 | 13.25 | | | | | |
| 1.1 μm | 3.95 | 12.93 | | | | | |
| 2.02 μm | 2.85 | 12.00 | 0.08 | 0.31 | 1.01 | 0.21 | 1.15 |
| 4-7 μm | 0.90 | 10.13 | | | | | |

postulated that the scattering of light was a function of particle size. Therefore, for the range of particle sizes investigated, wavelengths of approximately 260 nm give the optimum resolution.

As a result, particle sizing by capillary chromatography is seen to be an efficient method for particles in the range of 8000 Å to 5 μm, and will be used for our pigmented systems, especially at the beginning of a dispersion. Although the resolution is not very good at the smaller particle size, particles in this range have a characteristic elution volume that is reproducible. For particles less than 8000 Å in size, capillary chromatography is not a perfect method for accurate sizing, because of poor sensitivity.

Let us also mention that forces other than those arising from the flow field may be operative because of the coiled configuration of the tube. Better separation of all size particles may result if the capillary tube is laid flat on the ground or uncoiled.

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Chapter 4

## Experimental Results and Discussion

### I. Introduction

It is of prime importance, before displaying the results obtained in this work, to focus our attention on the type of pigmented system used and on the several problems encountered during the preparation of the samples which were finally injected into the chromatographic systems.

As a second part of this chapter, results from five different methods for assessing pigment dispersion will be described as a function of the milling time. As standard methods, we have chosen first the NPIRI grind gauge for a quick and easy check-up, followed by a much more accurate method using the electron microscope. Pictures on the behavior of our pigmented system as the milling time increases, and thus the dispersion is enhanced, will therefore be provided. A third method, using the color strength of the dried film, will also be mentioned and used as a standard. The results were obtained from parallel studies performed in this laboratory (4.1).

These standard methods will serve as a comparison to discuss the results obtained from the measurements carried out on the basis of the two chromatographic methods previously described. In the HDC method, two different average sizes of the packing beads will be used, respectively, 20 and 60 $\mu$m. In each of these three chromatographic methods, a calibration curve is provided.

### II. Description of the type of pigmented system used

Since these chromatographic methods were used on the basis

primarily of water-based systems, our main interest was to apply these methods for the measurement of particle size distribution of pigments in the case of water-based flexographic inks.

Water-based inks [4.2,4.3,4.4,4.5] have been used in flexographic printing for more than 25 years. They have been used commercially mainly for printing corrugated boxes, paper bags and multi-wall sacks. Even, increased attention, especially nowadays, has been given to developing water-based resins for printing of plastic packaging substrates [4.6]. With the absorbent substrates, the requirements have been for low cost producing a serviceable print finish, with no demand for a high gloss or special resistance properties. For these inks there has been a trend away from the conventional vehicles based on aqueous solutions of alkali-solubilized shellac and rosin maleates to the use of resin media derived from petrochemical sources. In recent years, the chemistry and technology of polymeric materials, poly(vinyl acetate) (PVA), poly(vinylidene chloride) (PVDC) and acrylic copolymers used for water-based paints has been exploited by resin manufacturers in the development of special media for use in printing inks. The newer types of water-based flexo inks have advantages over the conventional inks chiefly in their faster drying and improved dry and wet rub resistance, properties which are essential for applications such as wallpaper printing. They are also superior to the aqueous shellac/maleate types, in solvent (water) release properties; this is manifested by faster setting and the absence of the intervening sticky stage, characteristic of many of the conventional types of aqueous inks.

There are many types of resins and polymers available for water-borne ink systems. Each must be measured in terms of its strengths and weaknesses. As shown in Table 4.1, these water-borne resins may be divided into three groups : water soluble or reducible resins; colloidal dispersions or solubilized resins; emulsions or aqueous dispersions. Each type contains a broad range of resins and polymers, and many resins and polymers are found in all three groups [4.7,4.8].

Table 4.1

Water-borne resin systems

(1) Water Soluble or Reducible Resins

- a. Natural Products
- b. Synthetic Products
- c. Modified Natural Products

(2) Colloidal Dispersions or Solubilized Resins

- a. Alkali-soluble
- b. Acid-soluble
- c. Nonionic Functionality

(3) Emulsions or Aqueous Dispersions

- a. Emulsion Polymerization Polymers
- b. Emulsifiable Resins and Polymers

This paper will take account of the use of alkali-soluble resins whose chemistry will be described.

Aspects of the chemistry and technology of water-based inks have been reviewed previously [4.9] and informative papers have been written on acrylics for water-based printing inks [4.10,4.11]. Another

useful contribution on the use of synthetic resin dispersion in aqueous printing inks is by Firmin (4.12).

Sauntson (4.10) described the preparation of the alkali-soluble type of acrylic copolymer made by copolymerizing a suitable acid monomer in the polymer. Alkali-soluble acrylics are furnished as emulsions, solids or solutions. The deposited films are still water soluble but become water insoluble when the alkali is removed. If volatile amines are used to increase the pH, the polymer salt can revert back to the water insoluble form by a combination of mechanisms. The main ones are volatilization of the amine and neutralization by acids in the paper stock (4.11). Alkali-soluble emulsion polymers, when converted to alkaline salts, become soluble in polar solvents -alcohols and glycols- as well as in water. Solution takes place when the carboxyl groups in the long polymer chain become ionized. Repulsion of like charges then causes the chains to separate and solubilize, similar to the dissolving of solid polymer in organic solvent except that in this case the solvent is alkaline water. This indicates that pH of the system is a very important factor influencing the final properties and form of the polymer.

The two-dimensional diagrams of Sauntson's paper (4.10) are shown in Figure 4.1, illustrating the conversion and the changes that take place when the pH is raised. The pipe cleaner models of Figure 4.2 illustrate the three-dimensional form. Raising the pH causes the chains in the polymer emulsion to separate and the polymer dissolves. Viscosity increases with solubilization and there is a transition from a milky white emulsion to an almost clear solution. There is an

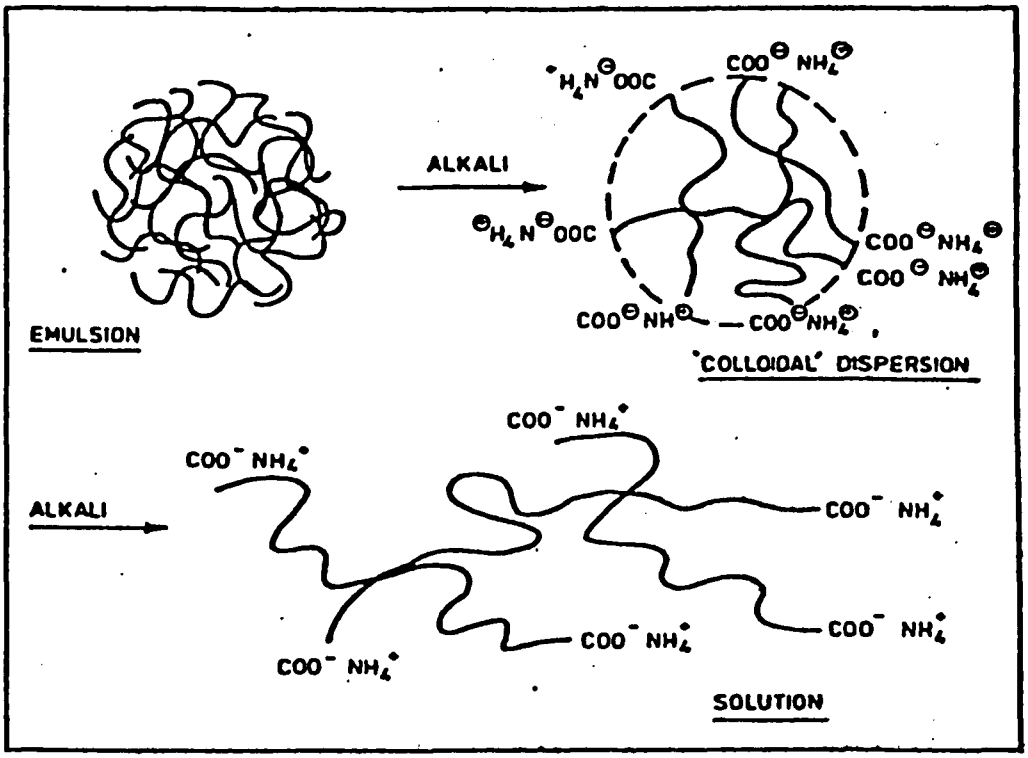



Figure 4.1

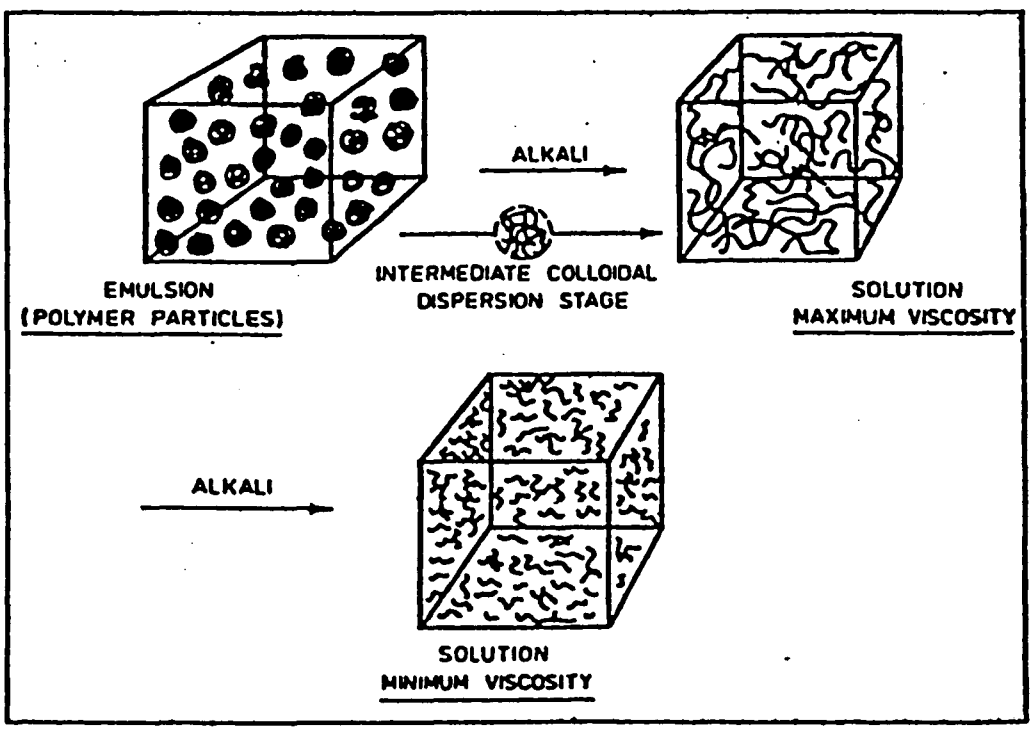



Figure 4.2

intermediate " colloidal dispersion " stage of partially neutralized polymer. In the process of neutralization, the viscosity of the system increases to a maximum due to chains opening to a rod-like configuration. As more alkali is added, the concentration of ions (e.g. $NH_4^+$) builds up and has a repressive effect on the ionization of the polymer chain. This results in some chain curling and a reduction in solution viscosity when neutralization is complete.

There could be also some practical problems, in that the viscosity is very dependent on pH at higher solids, making viscosity control very difficult. Use of organic co-solvent in the preparation of the water-soluble copolymers affects viscosity, drying rate, stability, pigment dispersion ability and flow. For example, addition of an alcohol such as isopropanol will speed up drying rate, reduce foaming tendencies and give lower viscosity at equal solids.

Concerning the type of base for the neutralization of the acid-modified polymer, the most volatile, such as ammonia, produce rapid development of water resistance in the film but press stability is minimized. Using less volatile bases such as medium-to-high boiling alkanol-amines from monoethanolamine to triethanolamine, morpholine or others, the press stability is improved but water resistance of the ink film is reduced as long as they remain in the film.

Finally, compared with conventional emulsion polymers having molecular weights ca 250,000 to 1,000,000 , the alkali-soluble copolymers used for printing inks have generally low molecular weights (10,000 to 25,000).

Let us emphasize also, that, in the formulation of water-based

flexographic printing inks, viscosity, flow, drying speed and film forming properties are greatly influenced by the type of copolymer, pH conditions, character of neutralizing base and the type and quantity of co-solvent. These factors also influence choice of pigments to be used. Because predominant solvent is alkaline water, it will be appreciated that even traces of acidity in a pigment can influence pH in such a way that stability is affected by viscosity changes.

III. Preparation of the samples

1. Formulation of the water-based flexographic inks

In all cases, the same vehicle was used, e.g. a styrenated acrylic resin, named " Joncryl 67 " from S.C. Johnson & Son, Inc., Racine, Wisconsin. This resin is sold as solid, water-white flakes with an acid value of 200 and a softening point of 290°F.

The vehicle solution was prepared and studied, as presented in Table 4.2 :

Table 4.2

Vehicle Solution

Content : 28% Joncryl 67

10% Ammonium Hydroxyde (28% $NH_3$)

62% Distilled Water

Aspect of the solution : transparent and viscous

Viscosity (Brookfield viscosimeter) = 280 cps at 60 rpm

Viscosity (Zahn Cup #2) = 110" at 22°C

pH (by pH meter) = 10.0 at 25°C

Two pigments will be studied, an inorganic and organic one, respectively. The inorganic pigment is a Medium Chrome Yellow #2343

from " The Harshaw Chemical Co. ", Cleveland, Ohio (primary particle size = 0.15 $\mu$m) while the organic pigment is a Diarylide Yellow (C.I. pigment 13) named as " 11-1300 Permanent Yellow GR ", from American Hoechst Corporation, Coventry, Rhode Island (primary particle size = 0.05 $\mu$m).

In order to avoid any foaming and to decrease the pH slightly (reaching pH 8.5), no more than 10% isopropanol was used. The pigment was added, finally, and mixed with the vehicle solution. Table 4.3 describes the formulations of both inks, in percent by weight.

Table 4.3

Formulation of both inks

| "Organic" water-based ink | "Inorganic" water-based ink |
|---|---|
| 15% Permanent GR | 31% Medium Chrome Yellow |
| 18% Joncryl 67 | 16% Joncryl 67 |
| 7% Ammonia @ 28% $NH_3$ | 6% Ammonia @ 28% $NH_3$ |
| 50% Distilled Water | 39% Distilled Water |
| 10% Isopropanol | 8% Isopropanol |
| ratio resin/pigment = 1.2 | ratio resin/pigment = 0.52 |

2. Type of equipment used for the grinding procedure

To study the effect of the milling time on the dispersion ability of these pigments, a vibration ball mill technique was carried out. These machines, which are manufactured, for instance, by the Red Devil Tools Co., were originally developed so that paints which are packed in tins and have formed a sediment can be homogenized without the need to open the tins.

The Red Devil, one of these machines, was used for our purpose.

It has a driving rod powered by an electric motor and equipped with two holders between which the container with the paint or mill base can be mounted by means of a threaded spindle [4.13]. The driving rod moves back and forth at a rate of 1350 reciprocating cycles a minute (other sources quote 1750 cycles), the container being turned through $15^{o}$ in an counter-clockwise direction during the forward movement and through $15^{o}$ in a clockwise direction on the return.

Because of this vigorous movement, this equipment can also be employed for dispersing pigments if grinding media are placed in the container together with the mill base. As is also the case with other modern ball mills, the level to which the grinding container is filled with mill base and grinding media, as well as the ratio of their volumes, one to the other, is of great importance. According to Doorgeest [4.14], the grinding containers used for shaking, unlike conventional laboratory and works ball mills, should be at least three-quarters full. Should they be less full than this, a " dead " zone occurs, which results in inadequate dispersion of the pigment. Another important factor is the influence of the viscosity of the mill base and, associated with this, the optimum pigment-binder-solvent ratio [4.15].

Vibration ball mills are, therefore, especially suitable for experiments in the laboratory and pilot plant, since in the dispersing containers used for these purposes there is no possibility of solvent losses due to evaporation, even at higher processing temperatures. According to data provided by Doorgeest [4.14], the saving in time in the dispersing of pigments compared with conventional ball mills is

90-95%, so that a dispersing time of one minute with a Red Devil corresponds to a dispersing time of one hour with a works ball mill; this is not in every case completely true, especially when using organic pigments.

In our case, the grinding media consists of glass beads (8 to 12 mesh). The level of the grinding media did not exceed one third of the entire mill base. It is difficult to know completely the internal mechanics of vibration milling, because of its complexity. There is no doubt, however, that vibration milling is carried out by nipping the particles between the grinding media. If the reader is interested in knowing the theoretical background of this process, he can refer to some work made by Tamura and Tanaka (4.16) who have attempted to ascertain with the aid of probability calculations the process taking place in the dispersing operation in the vibration ball mill.

3. Problems encountered during the dilution process

Once these two inks were prepared, and in order to reach the pigment concentration suitable for the use of chromatographic methods, some dilution problems arose. Indeed, it is better not to exceed 0.01% pigment concentration, which represents a very high dilution. Therefore, in order to avoid as much as possible some dilution shock, it was decided to dilute our inks step by step. The use of only distilled water as a diluent was not satisfactory; flocculation occured quite rapidly, and after two months, a complete breakdown of the dispersion was noticed.

Consequently, both these inks were diluted stepwise with the eluting solution, made of 0.001 M SLS in water, and the concentration

of the pigment was kept at the level of 0.01% for each sample. Table 4.4 gives for both pigments their exact concentration, together with the concentration of the vehicle. These diluted inks, even after a few months, are quite stable; some slight flocculation occurs, but the inks can be readily redispersed.

Table 4.4

Concentrations of the diluted samples

| "Inorganic sample" | "Organic sample" |
|---|---|
| 0.00908% Medium Chrome Yellow | 0.01125% Permanent GR |
| 0.00476% Joncryl 67 | 0.0135% Joncryl 67 |

## IV. Measure of the pigment particle size by the NPIRI grinding gauge

### 1. Description of the gauge

This recommended production gauge has been designated as the NPIRI Production Grindometer from " Precision Gage & Tool Co., Dayton, Ohio, and is shown on the right in Figure 4.3 . It is a very simple gage consisting of only a machined block and an Adco scraper. The grooves are one inch wide and one mil (25.4 $\mu$m) deep at the top. This depth range is considered to be the most useful for ink work, but deeper grooves are available on request. The wide paths constitute an important advance over the paint gages since they greatly increase the reproducibility and hence the reliability of the readings.

It will be observed that the grooves are cut completely off the end of the block instead of stopping at the tenth scale division. This feature allows full utilization of the deepest sections of the paths. The tapered paths are marked off at ten points which are numbered from one to ten according to the depth at that point in ten

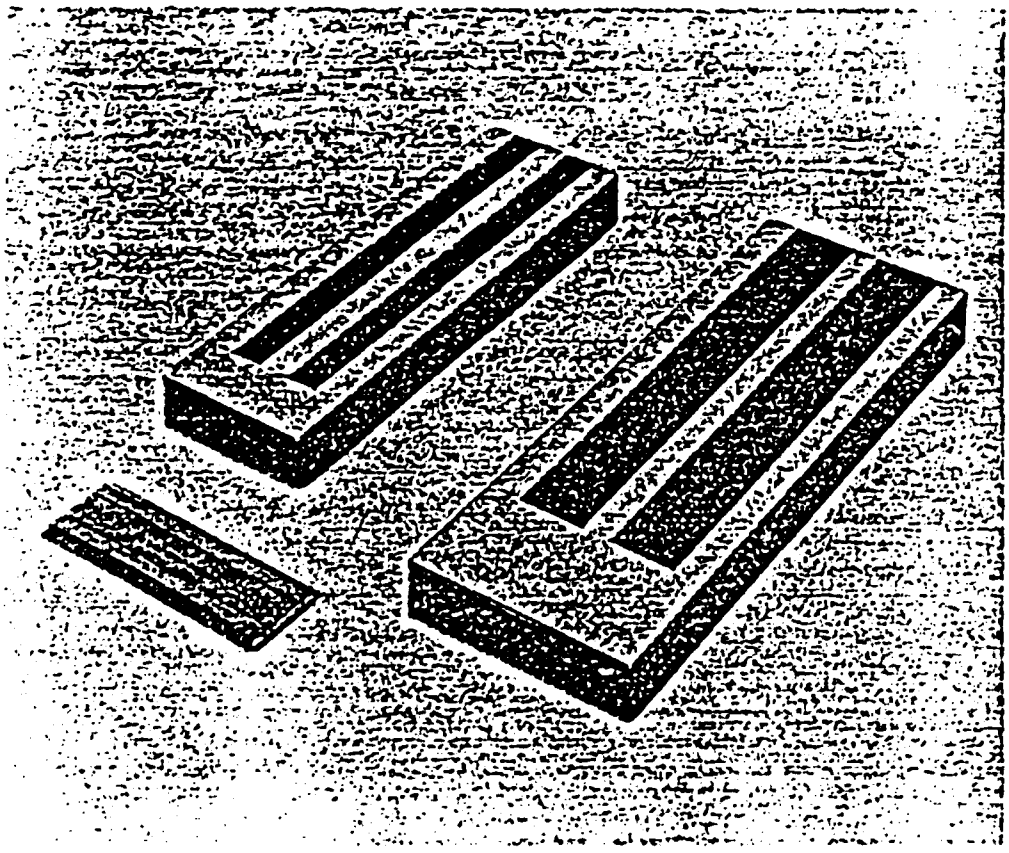


Figure 4.3 Adco scraper, small ink gauge and NPIRI Production Grindometer.

thousands of an inch.

The Adco scraper is inexpensive and has two useful edges which are rounded to a ten mil radius. This rounded edge decreases the effect of differing blade angle over a limited range in the hands of various operators and also it wears less rapidly than would a sharp edge.

2. Use of the NPIRI grind gauge

The operation is simple and rapid and consists of the following steps :

a. The scraper and block are very carefully cleaned.

b. The ink samples are placed at the deep end of the grooves.

c. The drawdown is made with the Adco scraper in a vertical position.

There are two drawdown patterns containing scratches which characterize the size and number of over-size particles in these two ink samples. There are two general methods which can be recorded and used for the evaluation of the samples. The first of these approaches is the counting of the number of scratches appearing or starting in a given section of the path. The second approach involves finding the first point in the path where a given number of scratches can be seen. The reading for this point on the scale at the side of the gauge is then taken as a measure of the fineness of grind. Since we use liquid inks, which evaporate quickly, it was decided to follow the second approach taking a measure each time we have at least two scratches. Even in this case, the readings were sometimes difficult to make.

3. Results obtained

Table 4.5 shows the NPIRI gauge readings for Diarylide yellow and Medium Chrome yellow, respectively, using the two-scratch method. These results show, indeed, that the readings do decrease with increasing milling time. They only give an idea on how good the dispersion is, but do not provide accurate measurements. Besides,

Table 4.5

Two-scratch NPIRI gauge readings

| Time of dispersion | Diarylide Yellow | | Medium Chrome Yellow | |
|---|---|---|---|---|
| | Gauge Reading | Particle size (μ) | Gauge Reading | Particle size (μ) |
| 0 min | 10 | 25.4 | 9 | 22.86 |
| 15 min | 4 | 10.2 | 4 | 10.0 |
| 30 min | ~ 3 | 7.5 | ~ 4 | 10.0 |
| 45 min | ~ 3 | 7.5 | ~ 4 | 10.0 |
| 1 h | 2 | 5.08 | ~2 | 5.5 |
| 2 h | 1.5 | 3.0 | ~1.5 | 3.5 |
| 4 h | < 1 | <2.0 | 1.0 | 2.54 |
| 6 h | < 1 | <2.0 | < 1 | <2.0 |
| 8 h | < 1 | <2.0 | < 1 | <2.0 |
| 10 h | ~ 0 | <1.0 | ~ 0 | <1.0 |
| 12 h | ~0 | <1.0 | ~ 0 | <1.0 |

the gauge readings are related to the biggest particles still present in the ink samples, and do not display an average particle size. The particles much larger than these sizes will not be recorded either; they will be dragged away by the scraper without forming any scratches.

V. Measurement of the average particle size by the three HDC columns

1. As mentioned earlier, this chromatographic system uses packed columns with beads of an average size of 20μm in diameter. Because of the limitations encountered in this method (a maximum particle

size of only 0.4 $\mu$m can be injected in this system), studies were made using only the Diarylide Yellow pigment.

A calibration curve was made, using polystyrene monodisperse latexes ranging from 380 Å to 3570 Å in particle size (Figure 4.4). The high values for $\Delta V$ indicate that good separations can be obtained, especially between 880 and 3570 Å. Table 4.6 shows the resolutions obtained with different mixtures of latexes of different particle size. The three-column HDC method gives higher resolution than the one column (the equation for the resolution is shown in Chapter 3, Section II.3).

Table 4.6

Resolution : R, HDC

| | Three columns | One column |
|---|---|---|
| 880/1760 | 0.62 | 0.41 |
| 880/2340 | 0.91 | 0.61 |
| 880/3570 | 1.45 | 0.94 |
| 1090/2340 | 0.71 | 0.49 |
| 380/880 | 0.33 | 0.23 |
| 380/1090 | 0.51 | 0.36 |
| 380/1760 | 0.95 | 0.64 |
| 380/2340 | 1.23 | 0.83 |
| 380/3570 | 1.78 | 1.17 |

2. The ink samples, diluted as described earlier, were injected, starting from the end of the dispersion, with much lower particle size. The eluant was the 0.001 M sodium lauryl sulfate solution in

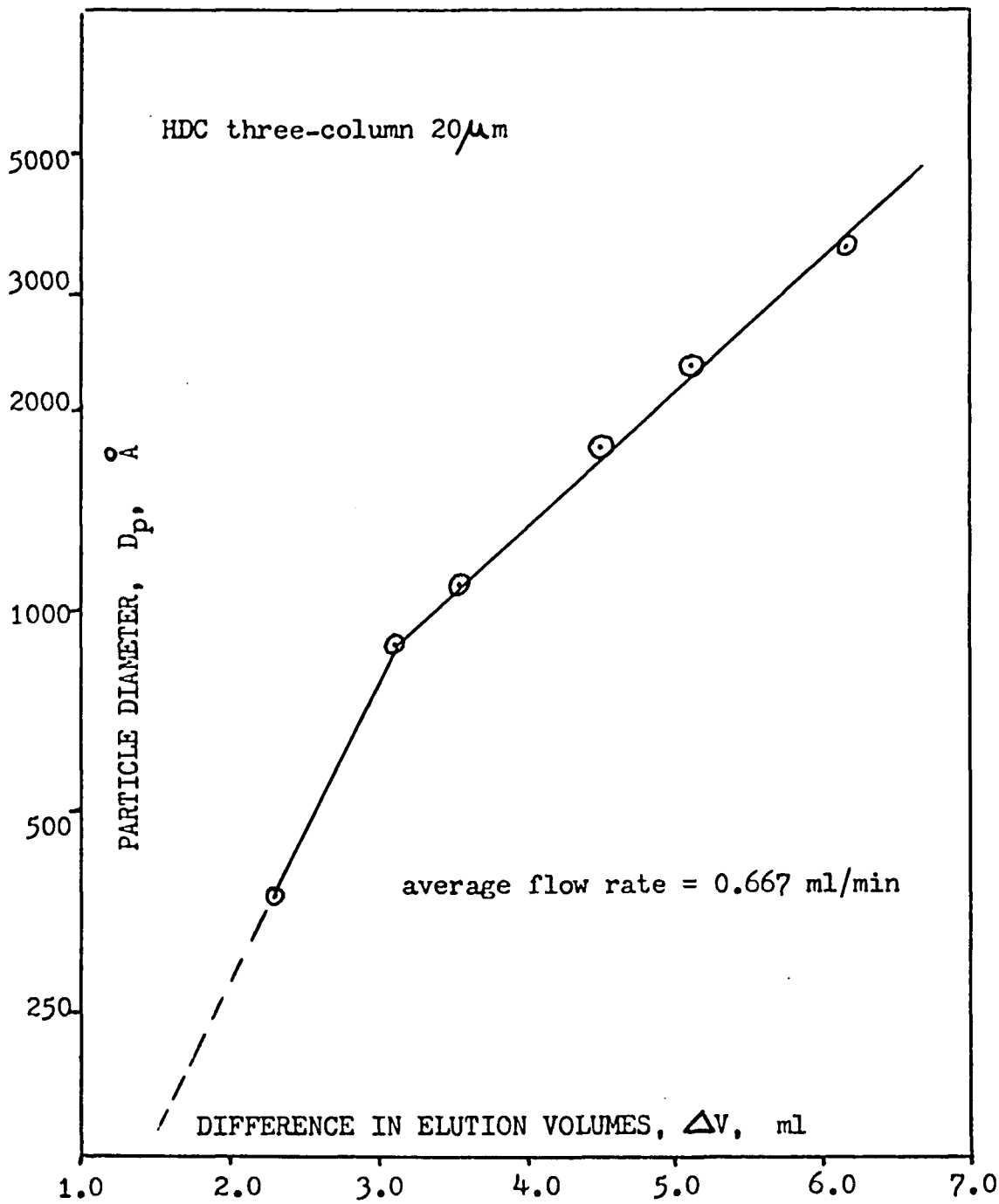



Figure 4.4 Calibration curve for the HDC three-column 20μm.

water. After two hours residence time, the chromatograms were recorded as shown in Figure 4.5 . The dotted line peak represents the samples containing the Joncryl 67 alone at a concentration of 0.014% in the sodium lauryl sulfate eluting solution (0.001 M SLS).

As can be seen, the pigments are separated from the vehicle solution. To make sure the small peak represents the Joncryl 67 vehicle, a sample of only Joncryl 67 in the eluting solution was separately injected and was recorded at the same time as this small peak (same $\Delta V$ as shown in Figure 4.7).

Table 4.7 shows the differences in elution volume and average particle sizes for the different ink samples. The values for both peaks are given. The optical density ranges are also displayed. The average flow rate was 0.67 ml/min . Figure 4.6 gives a plot of the average particle size versus time of dispersion. Most of the points are rather scattered, but, at least, there is a trend towards a decrease in particle size with the milling time. However, the results obtained at the beginning of the dispersion can not be taken into account due to the fact that most of the pigment particles in this range have a particle size higher than the maximum required for this HDC method. Indeed, after a few injections of these ink samples, some yellow sediments were observed at the top of the packed column indicating that most of the particles are retained. A measure of the percentage recovery will be described later in this chapter.

Figure 4.7 describes the effect of the milling time on the difference in elution volume, $\Delta V$, for both the big and the small peaks. As a result, we realize that, though the big peak shows a

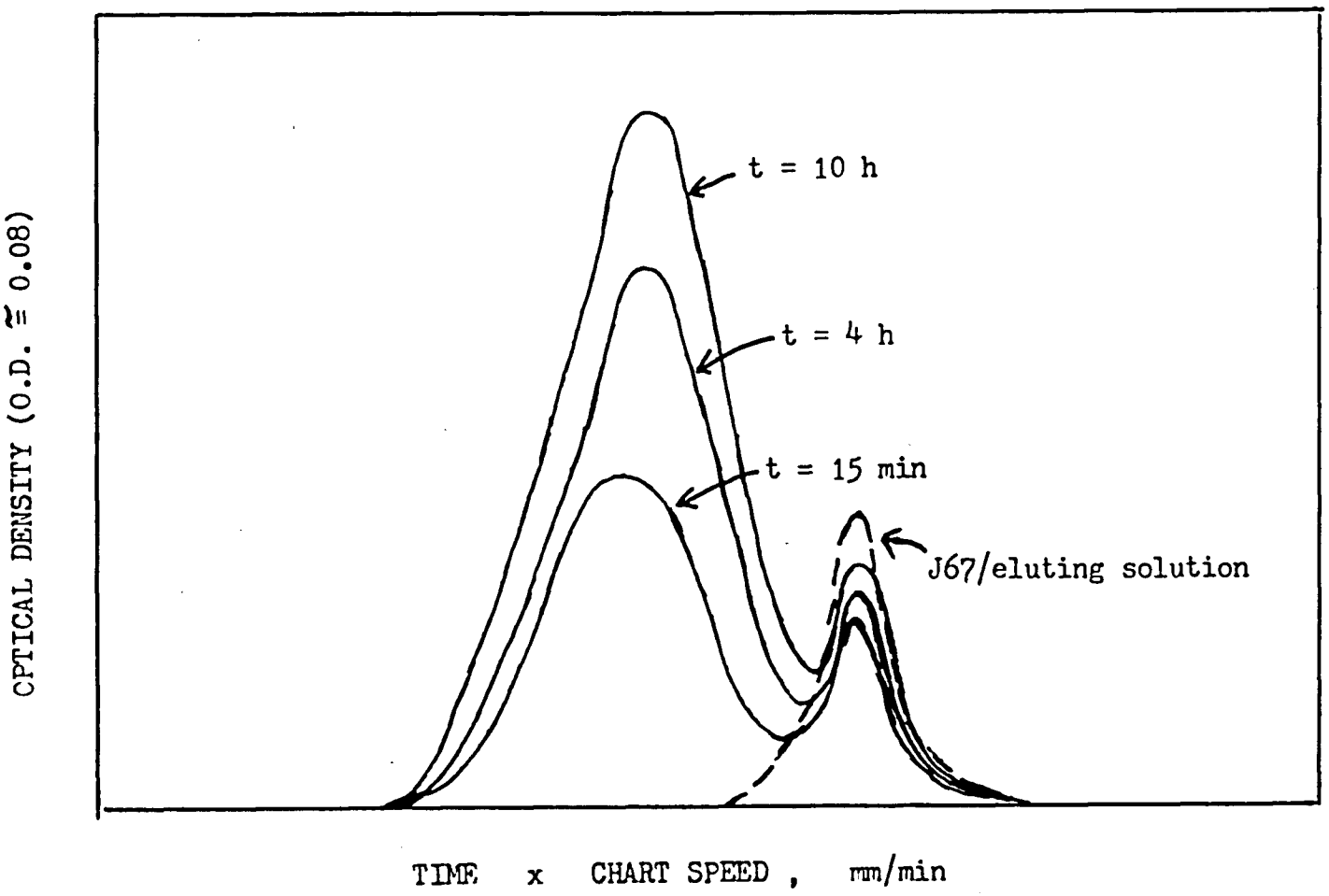



Figure 4.5 HDC 20 μm chromatograms at various times of dispersion (Diarylide Yellow) (chart speed = 10 mm/min).

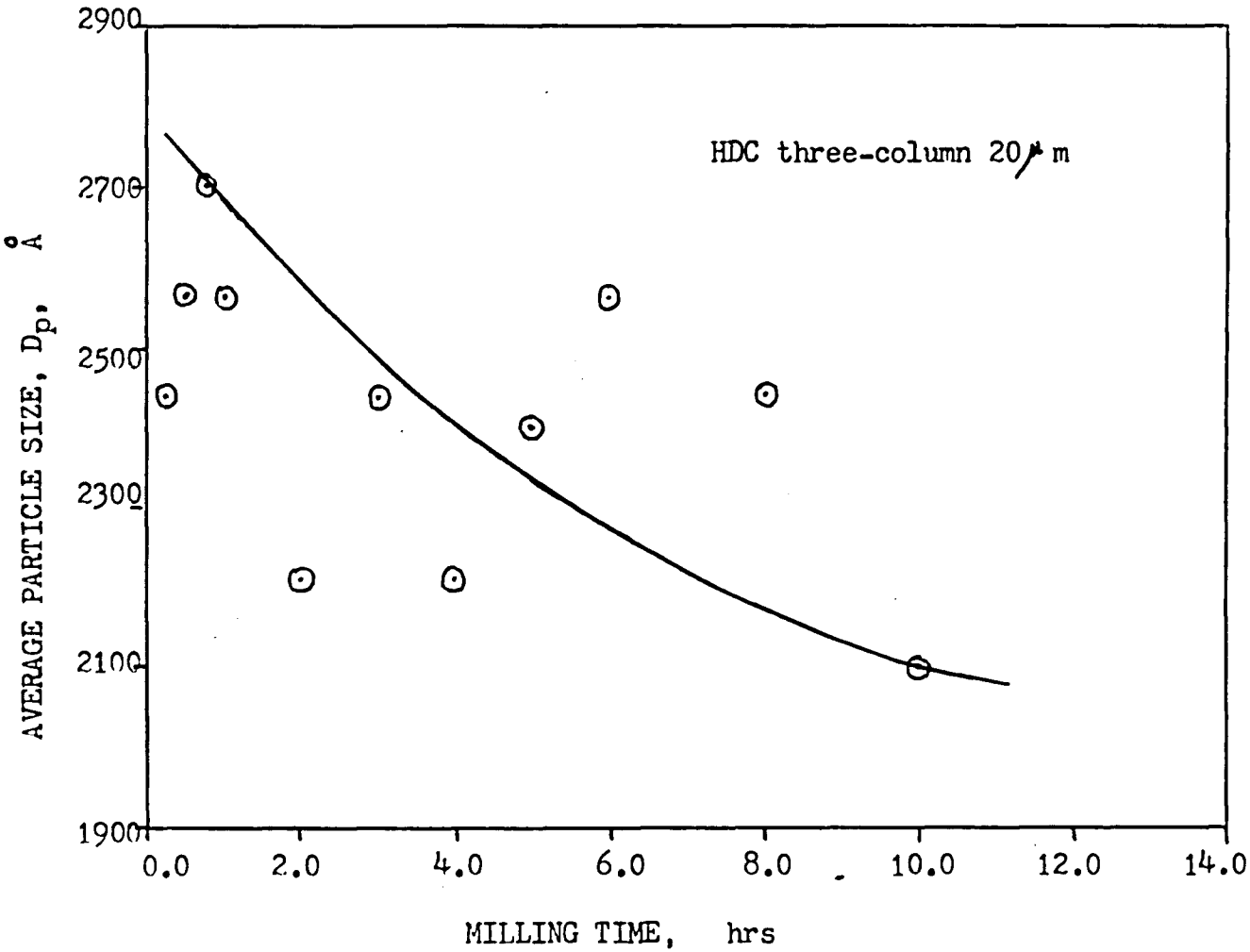



Figure 4.6 Average particle size as a function of time of dispersion for pigment Diarylide Yellow.

Table 4.7

Average particle size (Diarylide Yellow)

| O.D. | Time of dispersion | $\Delta V$ (ml) (Fig.4.7) big peak | $\Delta V$ (ml) (Fig.4.7) small peak | $D_p$ (Å) (Fig.4.6) pigment |
|---|---|---|---|---|
| 0.04 | 15 min | 5.31 | 0.955 | 2441 |
| 0.08 | 30 min | 5.514 | 1.19 | 2566 |
| 0.08 | 45 min | 5.6 | 1.136 | 2697 |
| 0.08 | 1 h | 5.454 | 1.12 | 2566 |
| 0.08 | 2 h | 5.14 | 1.132 | 2208.5 |
| 0.08 | 4 h | 5.23 | 1.13 | 2210 |
| 0.08 | 6 h | 5.5 | 1.193 | 2566 |
| 0.08 | 8 h | 5.363 | 1.04 | 2441 |
| 0.08 | 10 h | 5.1 | 1.05 | 2100 |
| 0.08 | J 67 sample | - | 0.97 | 75 |

decrease in $\Delta V$ with the milling time, with the small one it remains fairly constant, at a value which corresponds to the $\Delta V$ for the Joncryl 67 sample.

The increase in peak height and area for the pigment seen in Figure 4.5 is observed graphically in Figure 4.8 and 4.9 , respectively. These results would indicate that, at longer time of dispersion, a trend towards more monodispersed behavior is observed. The areas under the curve were measured by the Carl Zeiss, Inc. Integrator.

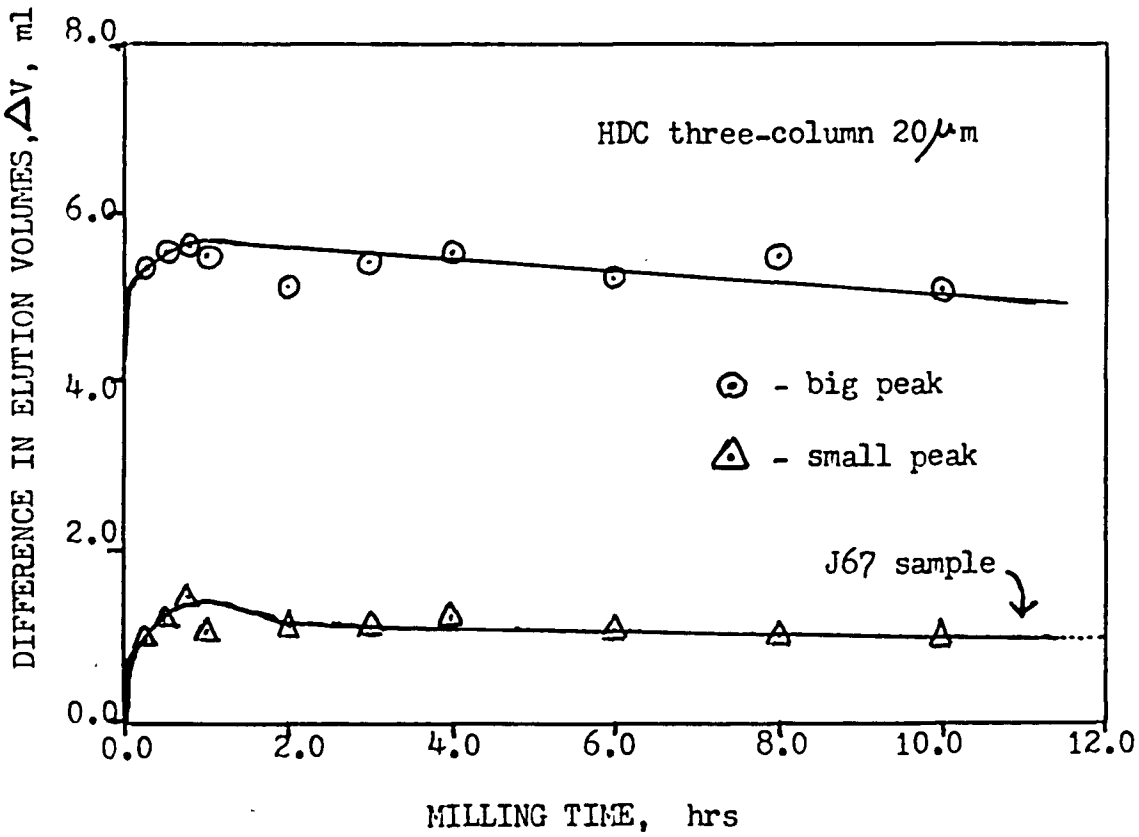



Figure 4.7 Effect of the milling time on the difference in elution volume ( $\Delta V$, J67 sample = 1 ml).

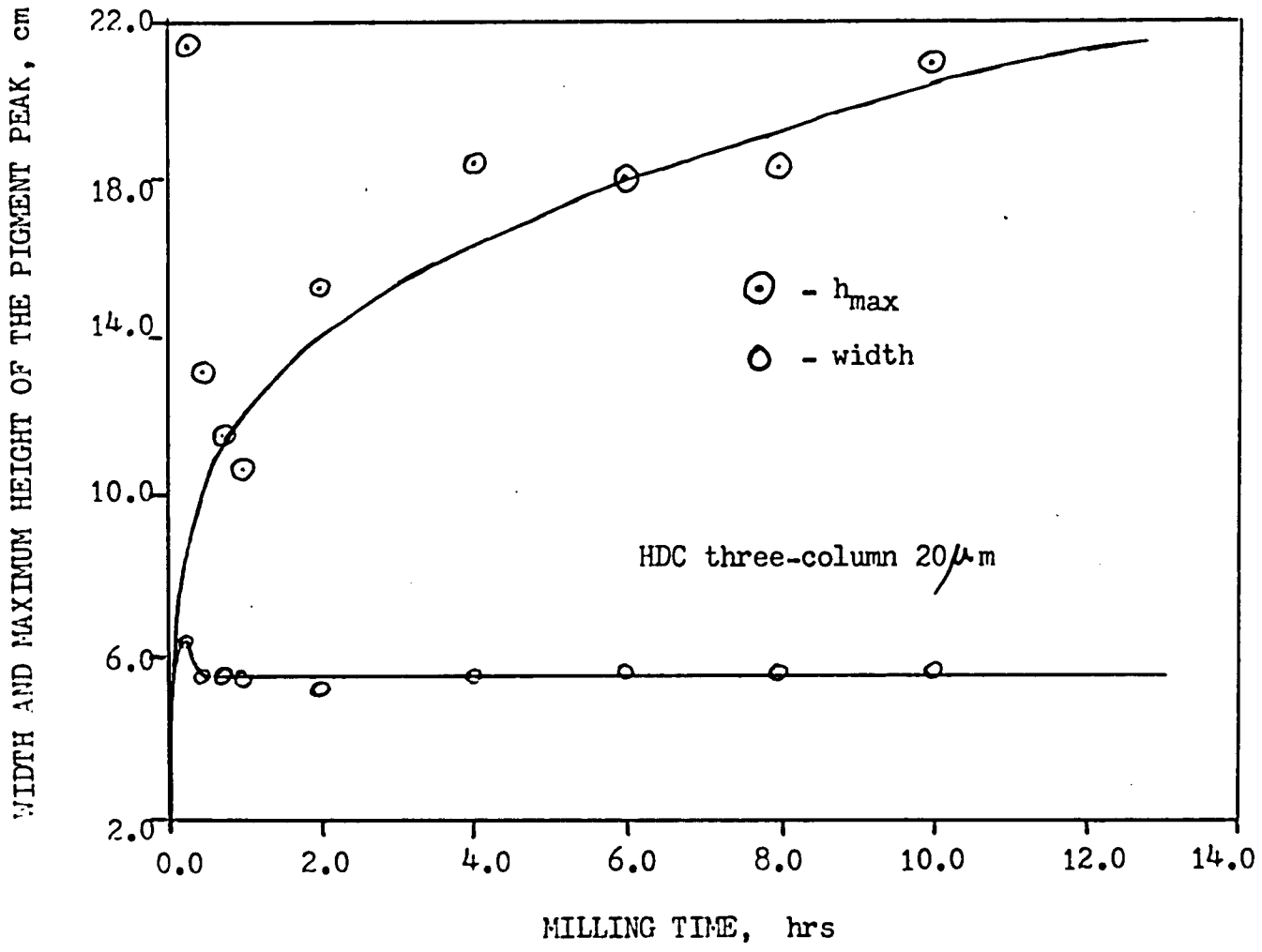



Figure 4.8 Effect of the milling time on the height and width of the pigment peak (Diarylide Yellow).

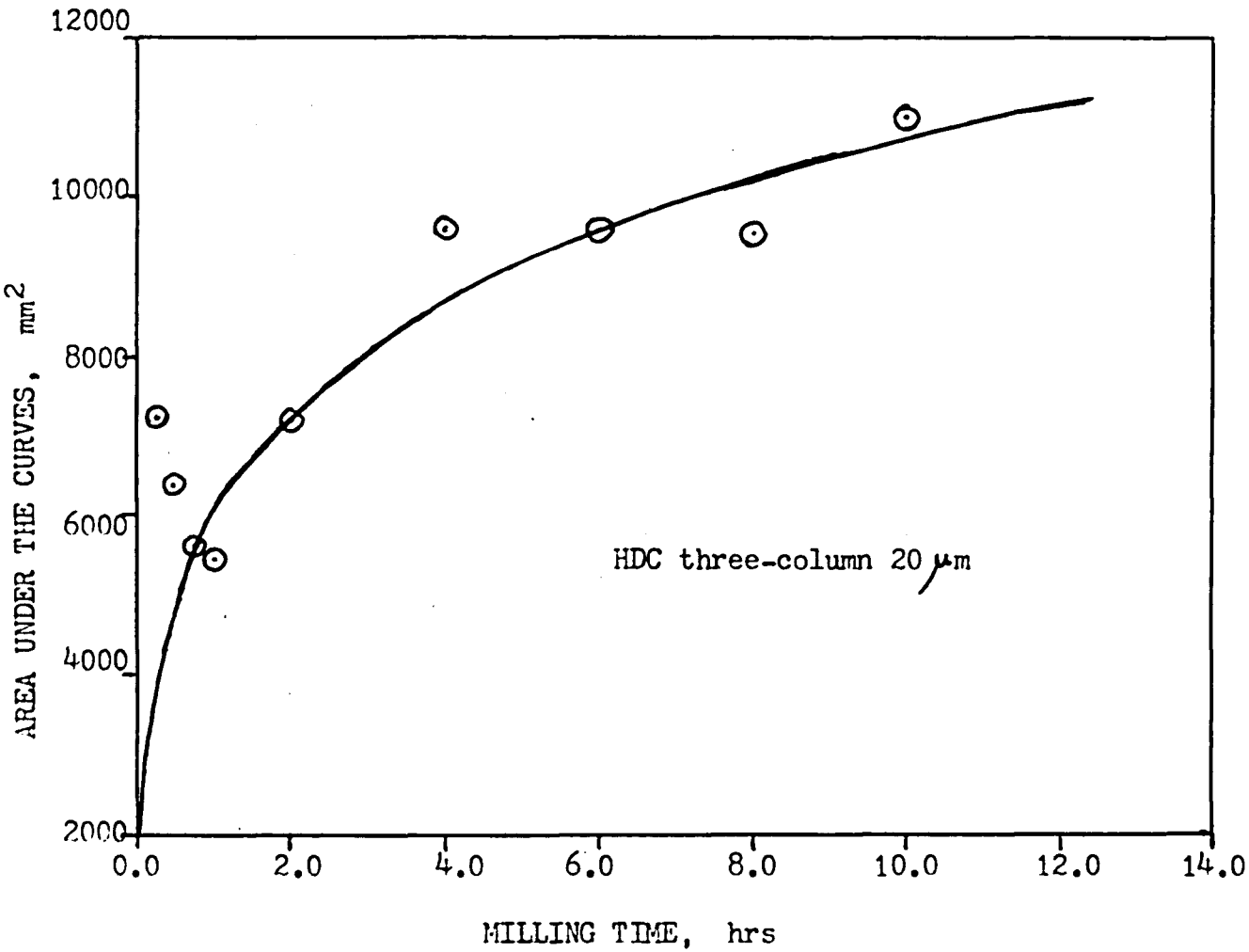



Figure 4.9 Dependence of the area under the pigment peaks on the milling time (Diarylide Yellow).

VI. Measurement of the pigment particle size by tubular pinch chromatography

Compared to the previous HDC method, the tubular pinch chromatography, as shown in Chapter 3, can be applied to higher-particle-size dispersions. Both Diarylide and Medium Chrome Yellow were studied.

1. Calibration curve

Various monodisperse latexes, with particle sizes ranging from 880 Å to 2.02 μm, were injected. The pressure, which was used for all this work, was around 2250 psi, giving a flow rate of 0.6 ml/min. Table 4.8 shows the differences in elution volume obtained and Figure 4.10 shows the calibration curve.

Table 4.8

Differences in elution volume, $\Delta V$

| O.D. | Particle size (Å) | Flow rate (ml/min) | d (cm) | t (min) | V (ml) | $\Delta V$ (ml) |
|---|---|---|---|---|---|---|
| 0.64 | Marker | 0.6 | 52.94 | 20.843 | 12.506 | - |
| 0.16 | 880 | 0.6 | 52.65 | 20.728 | 12.437 | 0.069 |
| 0.64 | 1760 | 0.6 | 52.3 | 20.59 | 12.354 | 0.152 |
| 0.64 | 2340 | 0.596 | 52.35 | 20.61 | 12.284 | 0.222 |
| 0.64 | 3570 | 0.596 | 51.94 | 20.449 | 12.19 | 0.316 |
| 0.64 | 4400 | 0.592 | 51.84 | 20.41 | 12.10 | 0.406 |
| 0.16 | 7940 | 0.6 | 50.55 | 19.9 | 11.94 | 0.566 |
| 0.16 | 11000 | 0.6 | 49.26 | 19.394 | 11.6364 | 0.870 |
| 0.16 | 20200 | 0.6 | 46.12 | 18.158 | 10.895 | 1.606 |

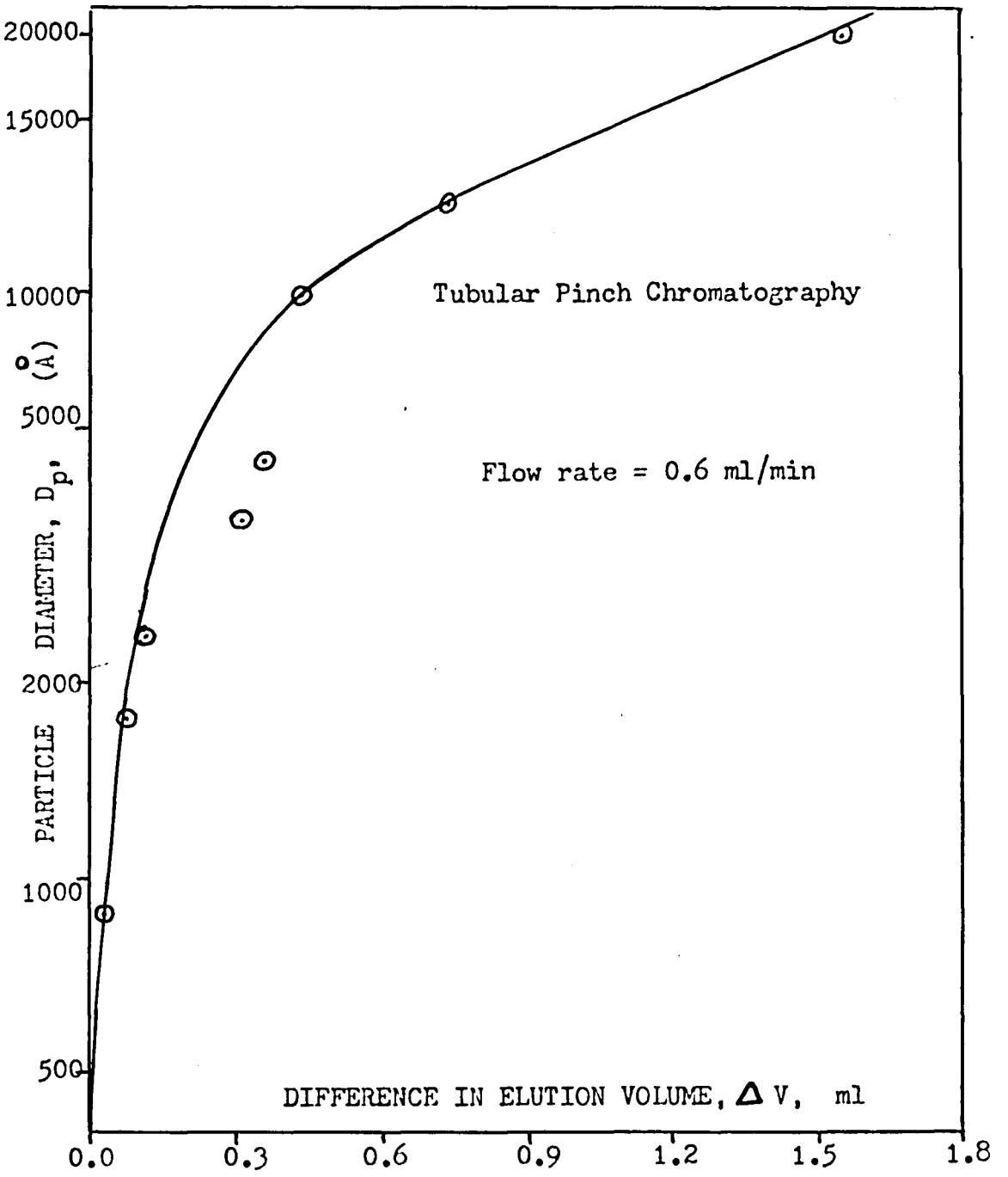



Figure 4.10 Calibration curve for the tubular pinch chromatography.

Under 3000 Å, the difference in elution volume is very small, but as the particle size is increased, and especially over 8000 Å, the separation is enhanced. Table 4.9 describes the resolutions for different pairs of monodisperse latexes and, as can be seen, the higher the particle sizes, the better the resolution.

Table 4.9

Resolution : Tubular pinch chromatography

| Sample #1 | Sample #2 | $R_{S1,2}$ |
|---|---|---|
| 2.02 μm | 1.1 μm | 0.316 |
| 2.02 μm | 7940 Å | 0.422 |
| 1.1 μm | 7940 Å | 0.110 |
| 1.1 μm | 4400 Å | 0.128 |
| 1.1 μm | 3570 Å | 0.162 |
| 1.1 μm | 2340 Å | 0.194 |
| 1.1 μm | 1760 Å | 0.212 |
| 7940 Å | 4400 Å | 0.020 |
| 7940 Å | 3570 Å | 0.054 |
| 7940 Å | 2340 Å | 0.086 |
| 7940 Å | 1760 Å | 0.102 |
| 4400 Å | 2340 Å | 0.063 |
| 4400 Å | 1760 Å | 0.079 |
| 3570 Å | 880 Å | 0.073 |
| 2340 Å | 880 Å | 0.041 |
| 1760 Å | 880 Å | 0.025 |

2. Results for the pigment Diarylide Yellow

Two ink batches were prepared, using the same concentration of pigment and the same formulation, but not at the same time. In each case, chromatograms such as those recorded in Figure 4.11 were observed. The peak for the Joncryl 67 sample could be only recorded when the vehicle solution was injected alone; otherwise, it is mixed with the polydispersed pigment sample. This effect is easily explained by the fact that the tubular pinch chromatography can only differentiate particle sizes which are at least higher than 2000 Å; at lower sizes, the resolution is very poor.

Table 4.10 describes the various differences in elution volumes with respect to the milling time for both batches, and their respective average particle sizes.

Table 4.10

$\Delta V$ and average particle size (Diarylide Yellow)

| Time of dispersion | Batch #1 | | Batch #2 | |
|---|---|---|---|---|
| | $\Delta V$ (ml) | $D_p$ (Å) | $\Delta V$ (ml) | $D_p$ (Å) |
| 15 min | 0.407 | 6003 | 0.430 | 6106 |
| 30 min | 0.370 | 5340 | 0.414 | 5902 |
| 45 min | 0.390 | 5599 | 0.391 | 5614 |
| 1 h | 0.360 | 5170 | 0.355 | 5080 |
| 2 h | 0.350 | 4999.5 | 0.399 | 5808 |
| 4 h | 0.310 | 4372 | 0.328 | 4675 |
| 6 h | 0.288 | 3993.5 | 0.294 | 4159 |
| 8 h | 0.240 | 3191 | 0.286 | 4024 |
| 10 h | 0.225 | 2467 | 0.211 | 2652 |
| 12 h | 0.190 | 2308.5 | 0.169 | 1964.5 |

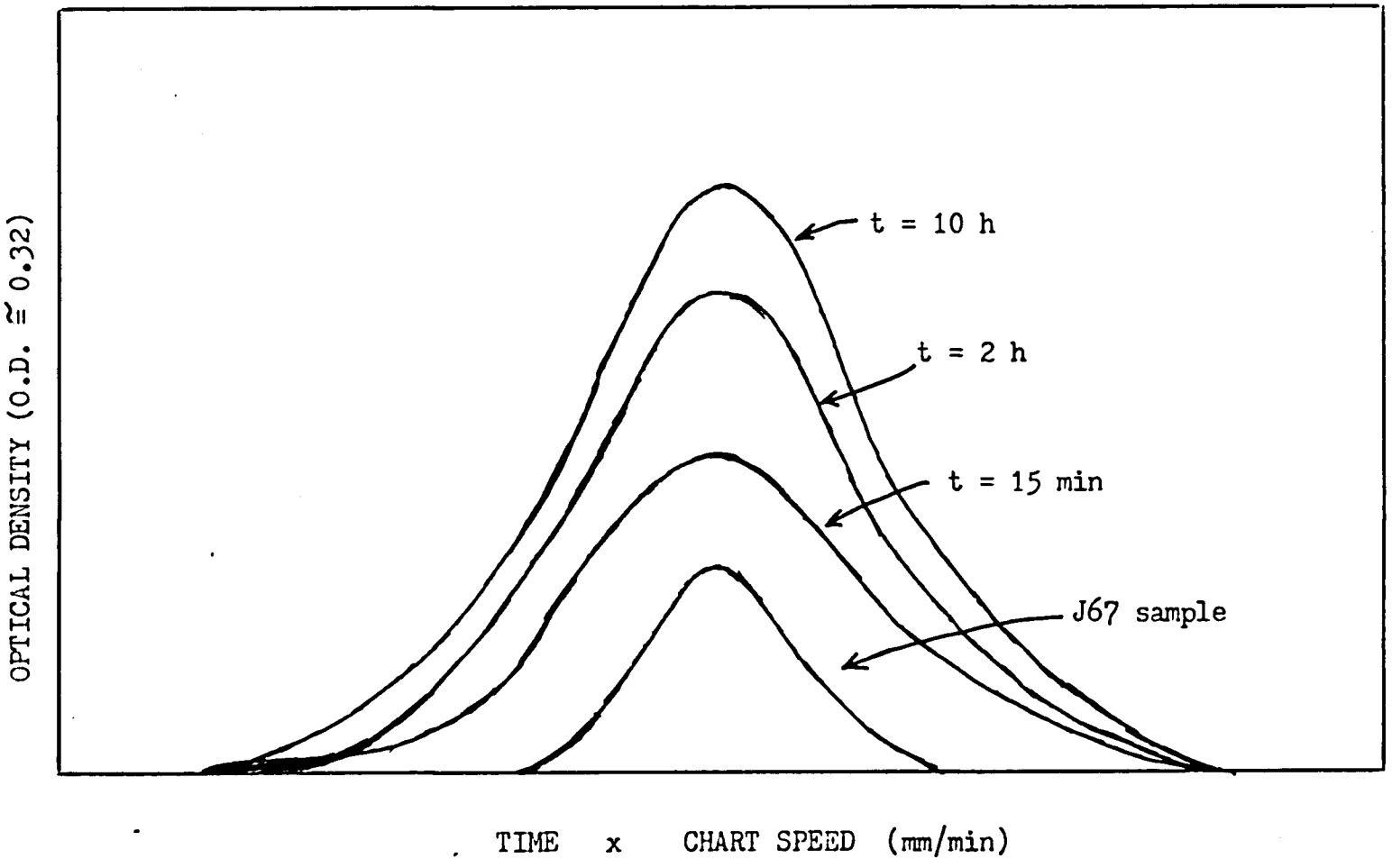



Figure 4.11 Tubular pinch chromatograms at various times of dispersion for the pigment Diarylide Yellow (chart speed = 25.4 mm/min).

In the case of the Joncryl 67 sample, the difference in elution volume is 0.02 ml, which corresponds to a particle size of about 400 Å. This value is indeed too high and not very consistent; and shows well the poor resolution which is got at these low sizes.

The results from Table 4.10 are then displayed in Figure 4.12 ; let us notice immediately the consistency from batch to batch, indicating that the Red Devil Shaker is a reproducible way of dispersing pigments in liquid inks. The curve obtained decreases gradually as the time of dispersion increases, and tends to level off after around 8 hours.

Figure 4.13 and 4.14 show the effect of the milling time on the peak's heights and their various areas. Again, we see a trend towards a certain narrower distribution, at the end of the dispersion.

3. Results obtained for the Medium Chrome Yellow

As we will see by the electron microscopy, this inorganic pigment has a rod-like shape; whereas in the case of Diarylide Yellow, organic pigment, the shape is more spherical. This could have an effect on the skewed peaks shown on the chromatograms in Figure 4.15 .

This chromatographic method, again, shows a consistent decrease in average particle size with the milling time. The results are presented in Table 4.11 , and the curve created from them is shown in Figure 4.16 . Again a gradual decrease is observed. Figure 4.13 shows then the effect of the milling time on the maximum height and width of the peaks for the Medium Chrome Yellow.

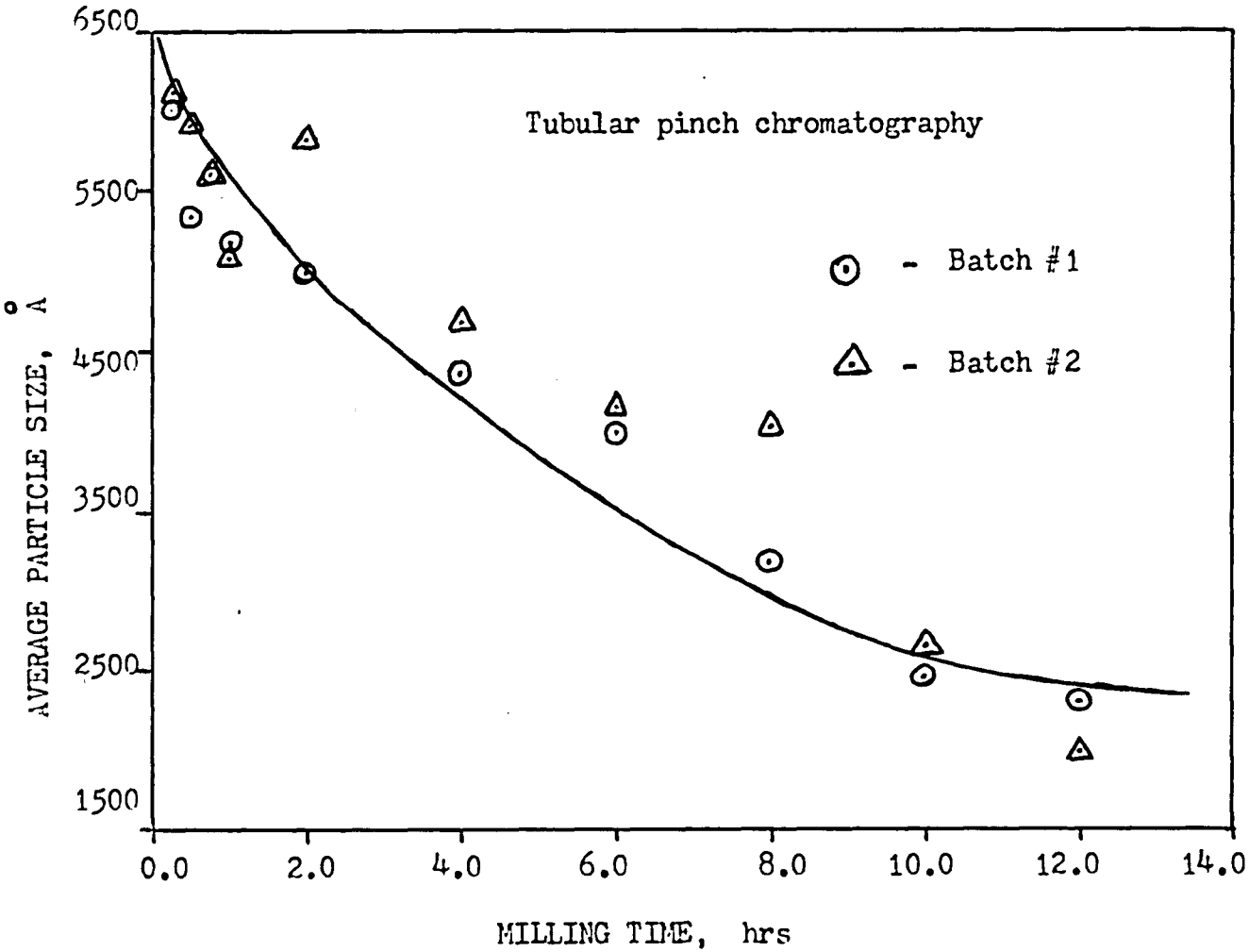



Figure 4.12 Effect of the milling time on the average particle size of Diarylide Yellow pigment.

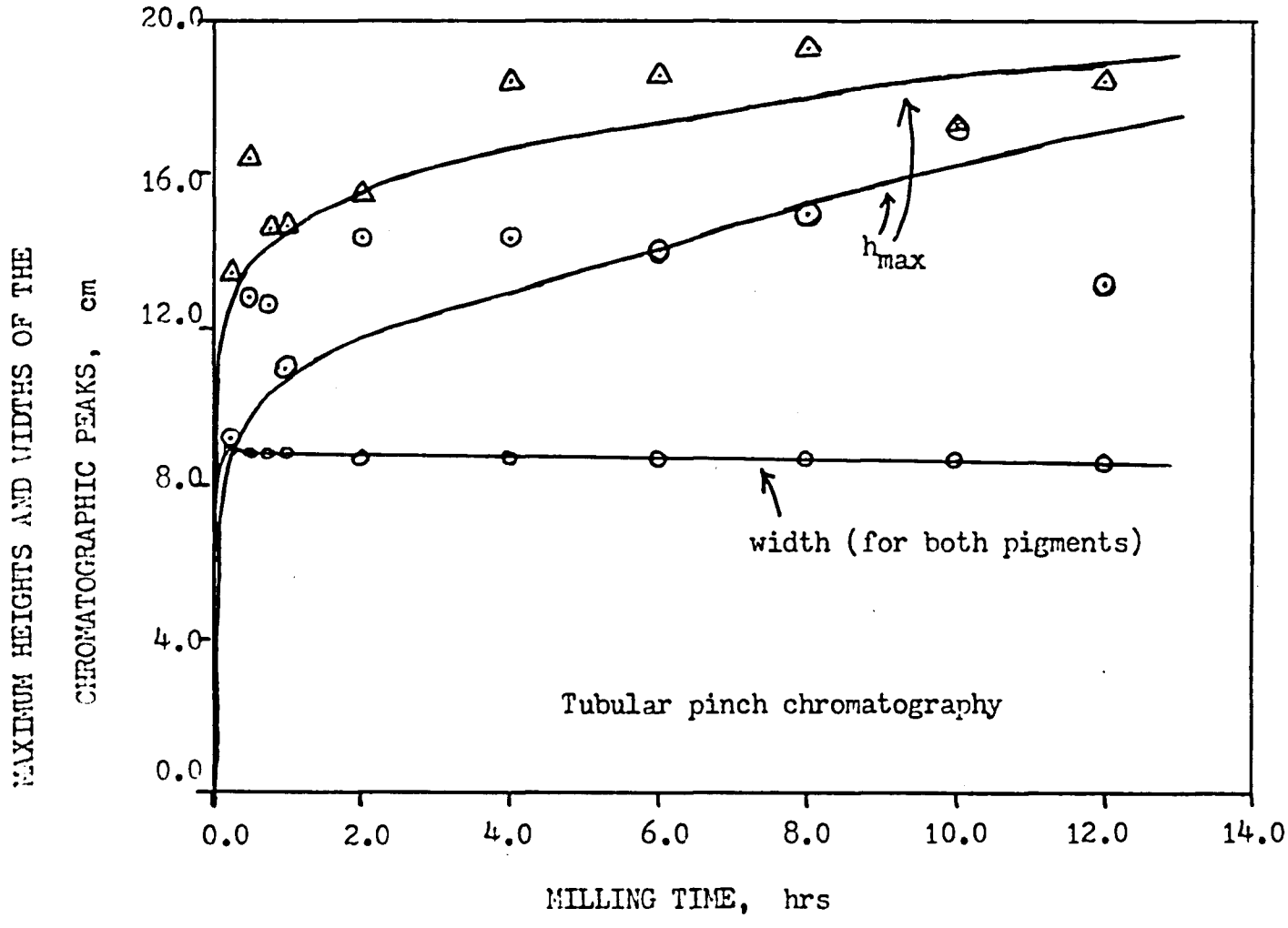



Figure 4.13 Effect of the milling time on the height and width of the peaks (⊙ - Diarylide Yellow; △ - Medium Chrome Yellow).

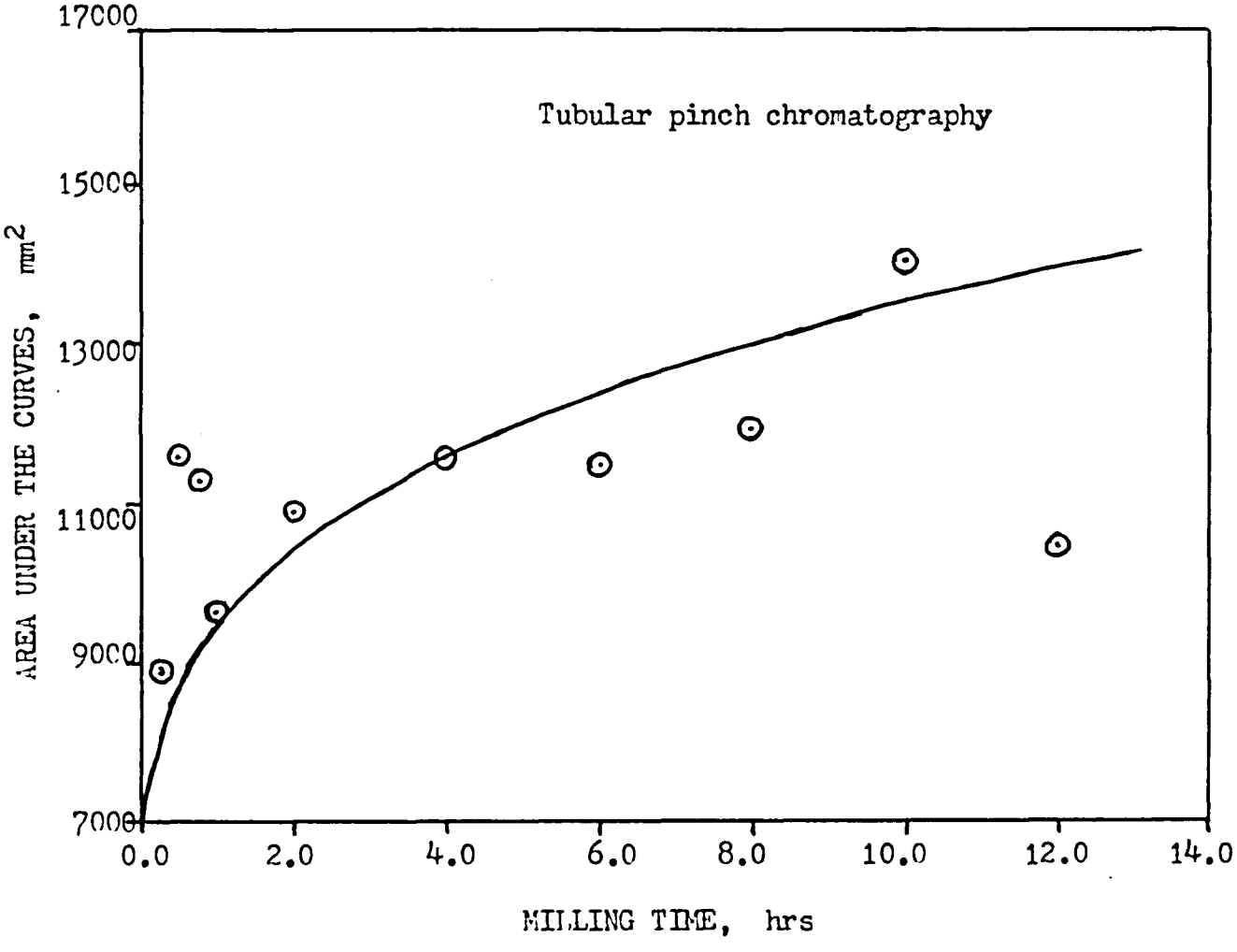



Figure 4.14 Effect of the milling time on the areas under the various peaks (Diarylide Yellow).

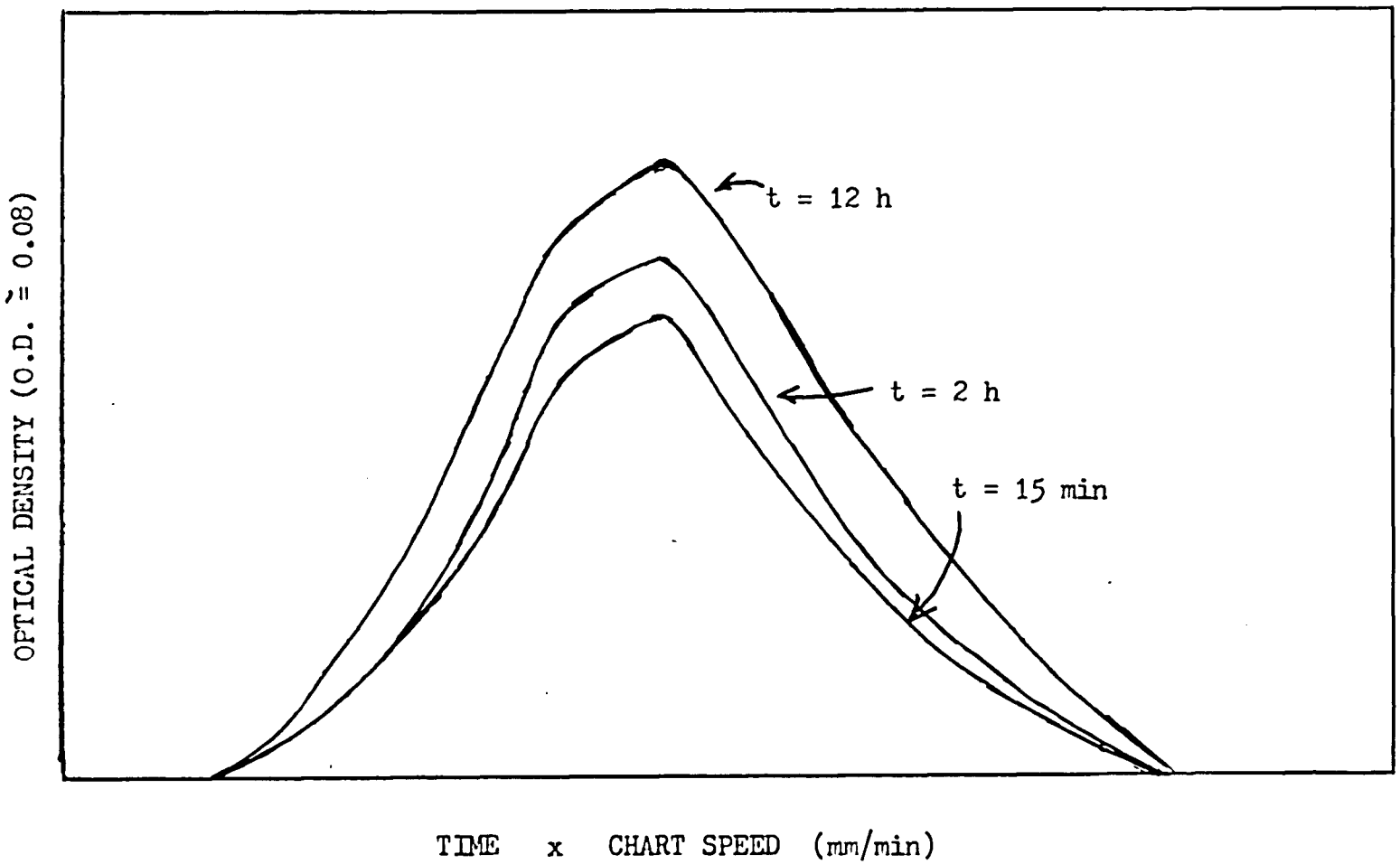



Figure 4.15 Tubular pinch chromatograms at various times of dispersion for the pigment Medium Chrome Yellow (chart speed = 25.4 mm/min).

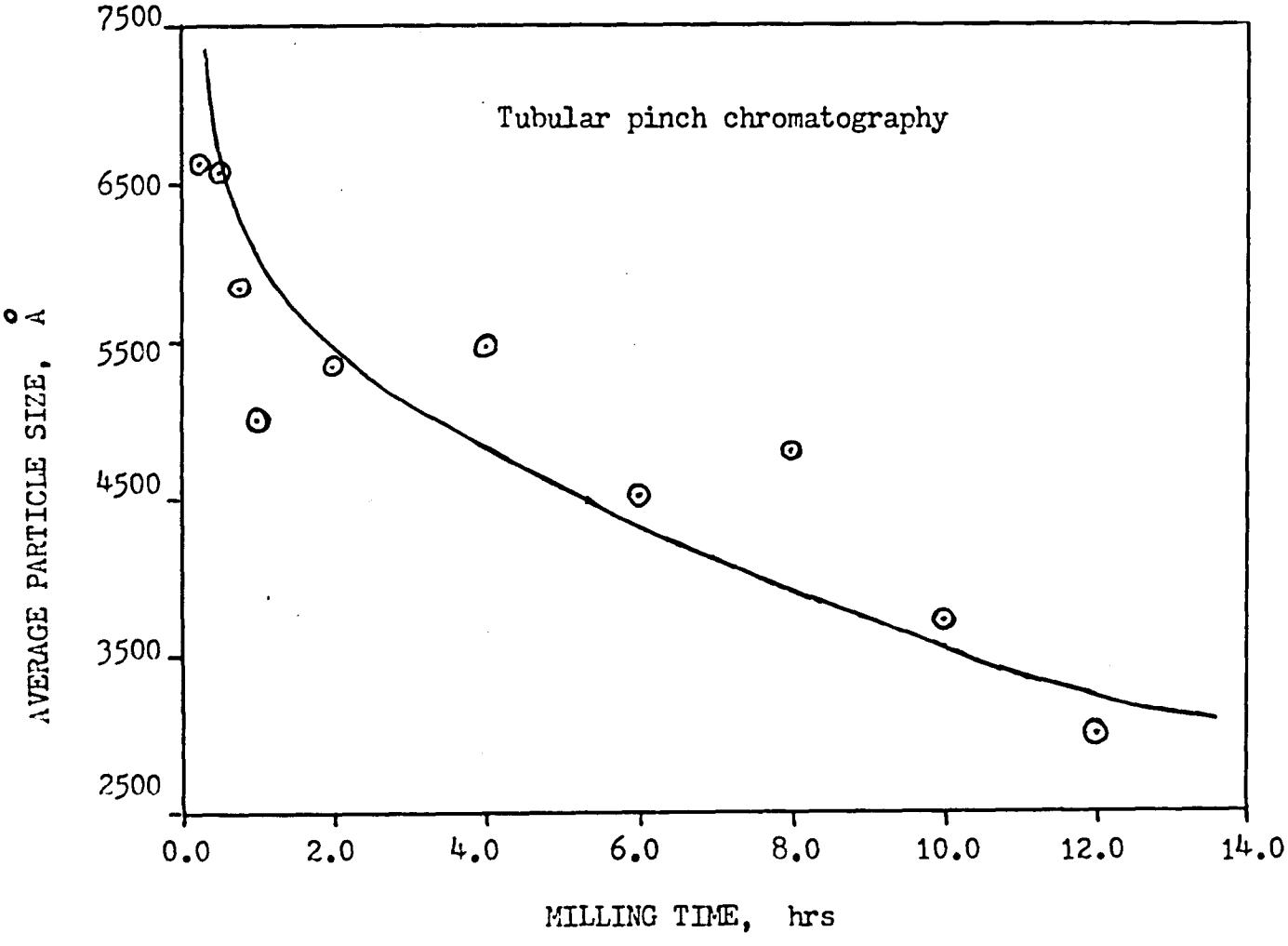



Figure 4.16 Effect of the milling time on the average particle size of Medium Chrome Yellow pigment.

Table 4.11

Differences in elution volume and average particle size
(Medium Chrome Yellow)

| Time of dispersion | $\Delta V$ (ml) | $D_p$ (Å) |
|---|---|---|
| 15 min | 0.463 | 6643 |
| 30 min | 0.459 | 6583.5 |
| 45 min | 0.415 | 5860 |
| 1 h | 0.348 | 5007.5 |
| 2 h | 0.372 | 5347 |
| 4 h | 0.384 | 5477 |
| 6 h | 0.319 | 4524 |
| 8 h | 0.336 | 4795.5 |
| 10 h | 0.273 | 3739.5 |
| 12 h | 0.227 | 3010 |

As in the case of Diarylide Yellow, the trend is to a narrower distribution at the end of the dispersion. The areas under the various peaks were also calculated (by Zeiss integrator) and recorded in Figure 4.17 .

Therefore, the results which were obtained by this chromatographic method show that we have available an interesting and reproducible way of measuring the particle size of pigments, either organic or inorganic. Usually, at the flow rate which was used, i.e. 0.6 ml/min, 20 minutes after injection the peaks are recorded. Besides, this tubular stainless-steel coil can be compared to a by-pass line, since there is no packing material inside; and, hence, all the samples are completely recovered, giving almost 100% recovery.

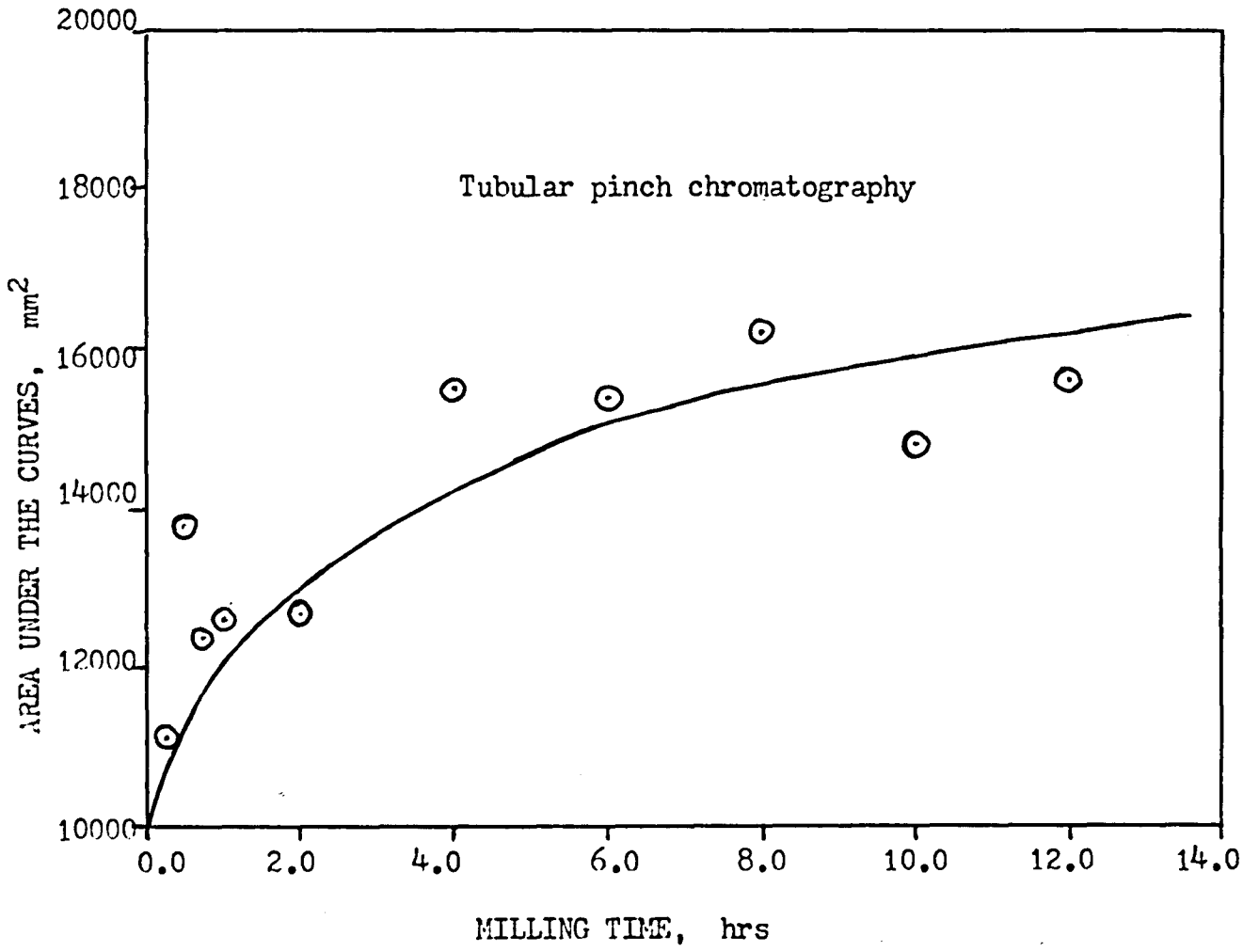



Figure 4.17 Effect of the milling time on the areas under the curves for pigment Medium Chrome Yellow.

VII. Measurement of the pigment particle size by an HDC column packed with beads of 60 μm average size

In order to avoid the limitations encountered with the previous HDC method, larger average-size beads were used. Figure 4.18 displays an optical microscope picture of the beads, taken after screening them through sieves of 200 mesh (74 μm) and 325 mesh (44 μm) respectively, in order to narrow their size distribution.

First of all, a glass column was packed by gravity with these new beads, using a method described in the Appendix. The peaks for the marker which were recorded, thereafter, were asymmetrical with a big shoulder at one end, showing a lack of perfectly compressed packing, and the appearance of some channelling.

A stainless-steel column of 80 cm long was, then, used. It allows us to reach pressure of around 2000 psi, since the inside diameter of these columns is much smaller, around 4.6 mm. The beads are, therefore, packed under much higher pressure and can be more easily compressed. A 5 μm filter is placed at the bottom of the column, retaining the packed beads in their right compressed position. Fourty ml of a 50% solid slurry is placed in a stainless-steel reservoir connected at the top of the column, in order to pack this column. This reservoir is then removed.

1. Calibration curve

Since the column is narrower, and only one column was used, a low flow rate had to be used. The pressure used was around 100 psi, giving a flow rate of 0.533 ml/min, which remained constant for all the injections, either latexes or ink samples.

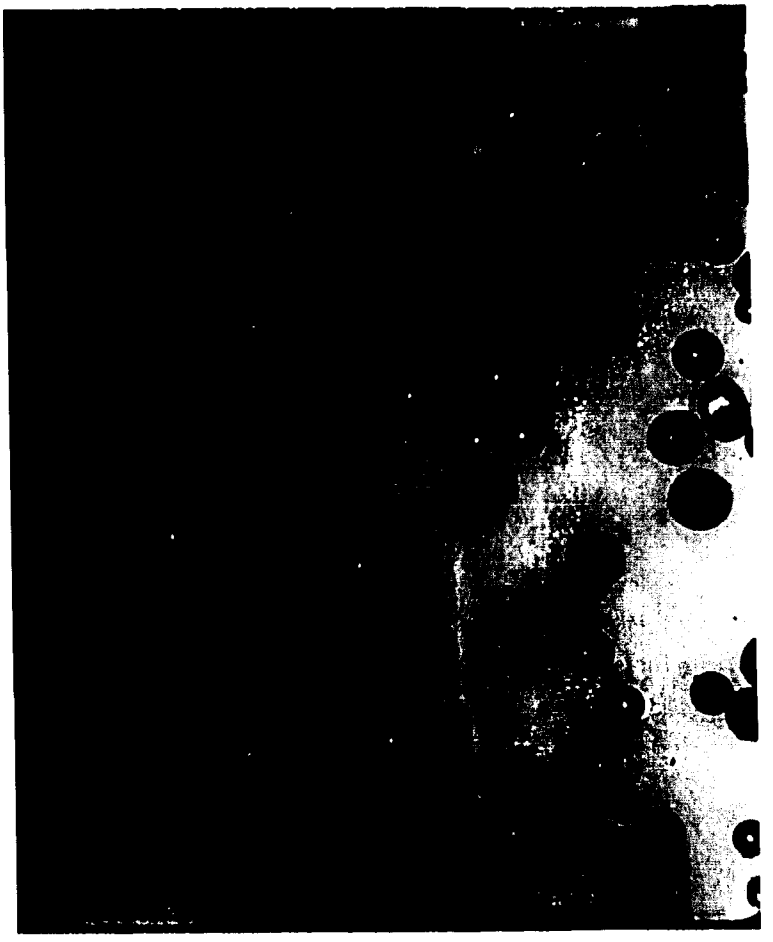


Figure 4.18 Optical microscope picture of styrene-divinyl-benzene copolymer beads with an average particle size of 60 $\mu$m (Magnification : 100X).

Table 4.12 describes the differences in elution volume for various monodisperse latexes, whose particle size range from 380 Å to 11,000 Å. Table 4.13 shows the resolutions obtained for different pairs which, usually, are low compared to the 20 μm packed columns.

Table 4.12

Differences in elution volume for SS-HDC 60 μm
(average flow rate = 0.533 ml/min)

| O.D. | Samples (Å) | d (cm) | t (min) | V (ml) | ΔV (ml) |
|---|---|---|---|---|---|
| 0.32 | Marker | 31.78 | 12.512 | 6.669 | - |
| 0.32 | 380 | 31.43 | 12.374 | 6.596 | 0.073 |
| 0.64 | 880 | 31.33 | 12.335 | 6.575 | 0.094 |
| 2.56 | 1760 | 31.20 | 12.284 | 6.5474 | 0.122 |
| 1.28 | 2340 | 30.95 | 12.185 | 6.495 | 0.174 |
| 1.28 | 3570 | 30.60 | 12.047 | 6.421 | 0.248 |
| 1.28 | 4400 | 30.80 | 12.126 | 6.463 | 0.206 |
| 0.64 | 7940 | 30.30 | 11.929 | 6.358 | 0.311 |
| 0.16 | 11000 | 29.95 | 11.790 | 6.284 | 0.385 |

In Figure 4.19, a calibration curve is shown with a change in the slope at about 1700 Å . The values of ΔV, compared to the previous methods, are much lower; this is related to the low values for the resolutions in Table 4.13 . Therefore, the separation between particles of different sizes is greatly reduced. It could be improved just by increasing the number of columns, allowing the particles to stay for a longer time.

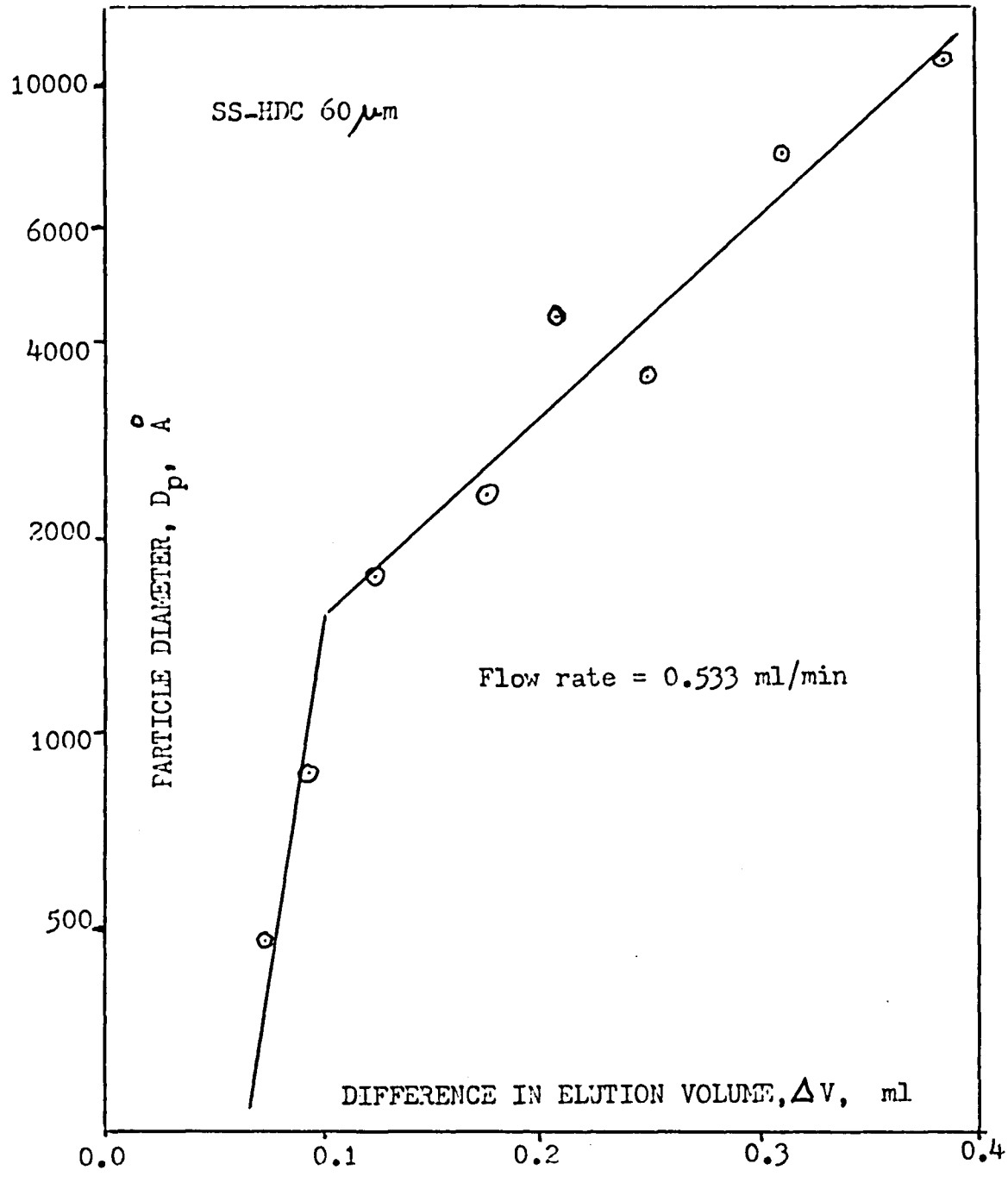



Figure 4.19 Calibration curve for the SS-HDC 60 μm column.

Table 4.13

Resolution : $R_S$ (SS-HDC 60 µm)

| Sample #1 (Å) | Sample #2 (Å) | $R_{S_{1,2}}$ |
|---|---|---|
| 11000 | 7940 | 0.06 |
| 11000 | 4400 | 0.12 |
| 11000 | 3570 | 0.11 |
| 11000 | 2340 | 0.158 |
| 11000 | 1760 | 0.203 |
| 7940 | 4400 | 0.06 |
| 7940 | 3570 | 0.053 |
| 7940 | 2340 | 0.098 |
| 7940 | 1760 | 0.142 |
| 4400 | 2340 | 0.04 |
| 4400 | 1760 | 0.07 |
| 3570 | 880 | 0.112 |
| 2340 | 880 | 0.069 |
| 1760 | 880 | 0.0233 |

2. Results for the Diarylide Yellow pigment

The chromatograms are shown for various times of dispersion in Figure 4.20 . These peaks were recorded only 12 minutes after injection and at the same flow rate we use to calibrate the column. Again, this chromatographic method doesn't separate the peak for the pigment from the one for the Joncryl 67 sample, since at low particle size, the resolution is very low, and the $\Delta V$ is very small.

Table 4.14 describes the differences in elution volume and

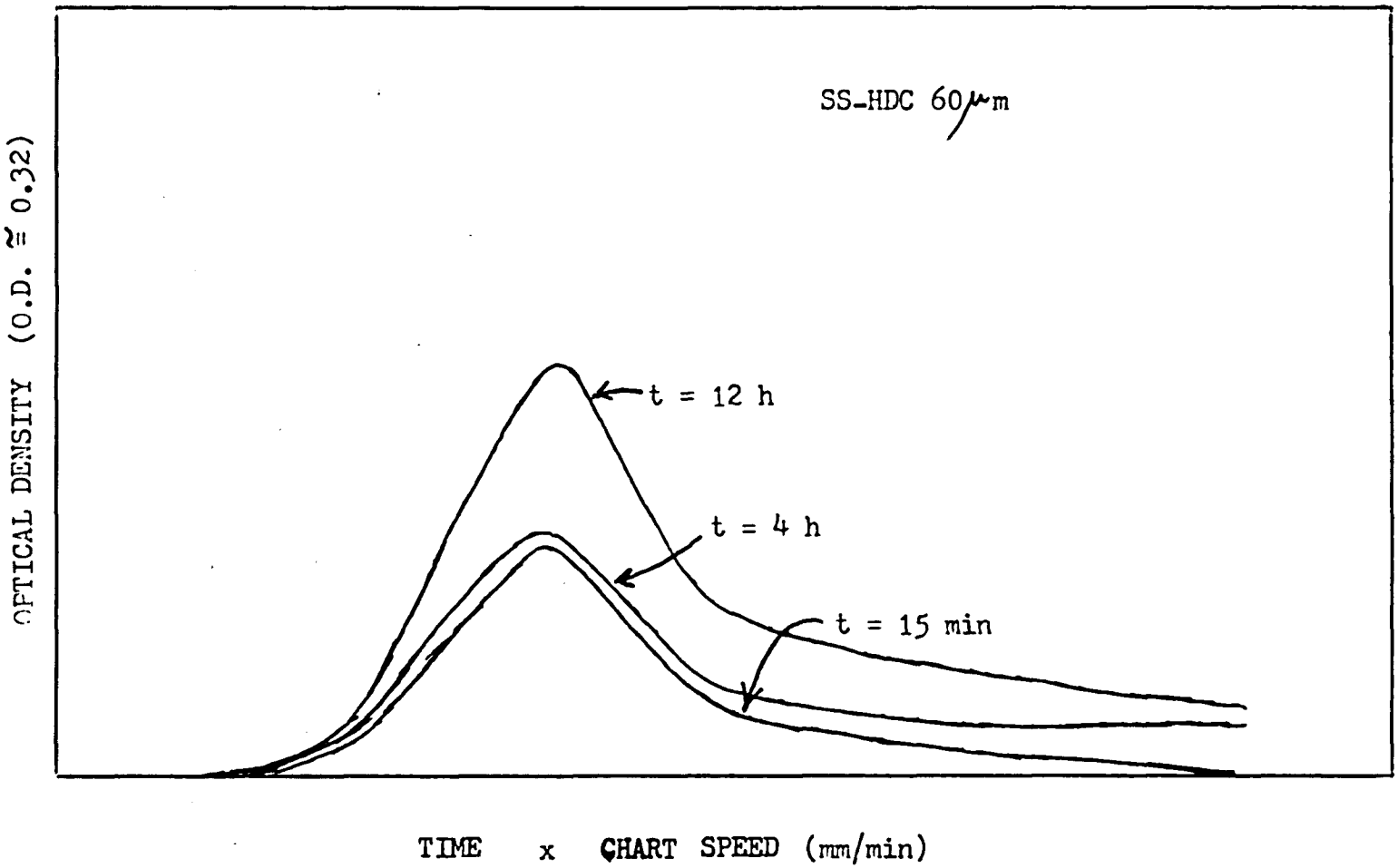



Figure 4.20 Chromatograms at various times of dispersion for Diarylide Yellow (chart speed = 25.4 mm/min).

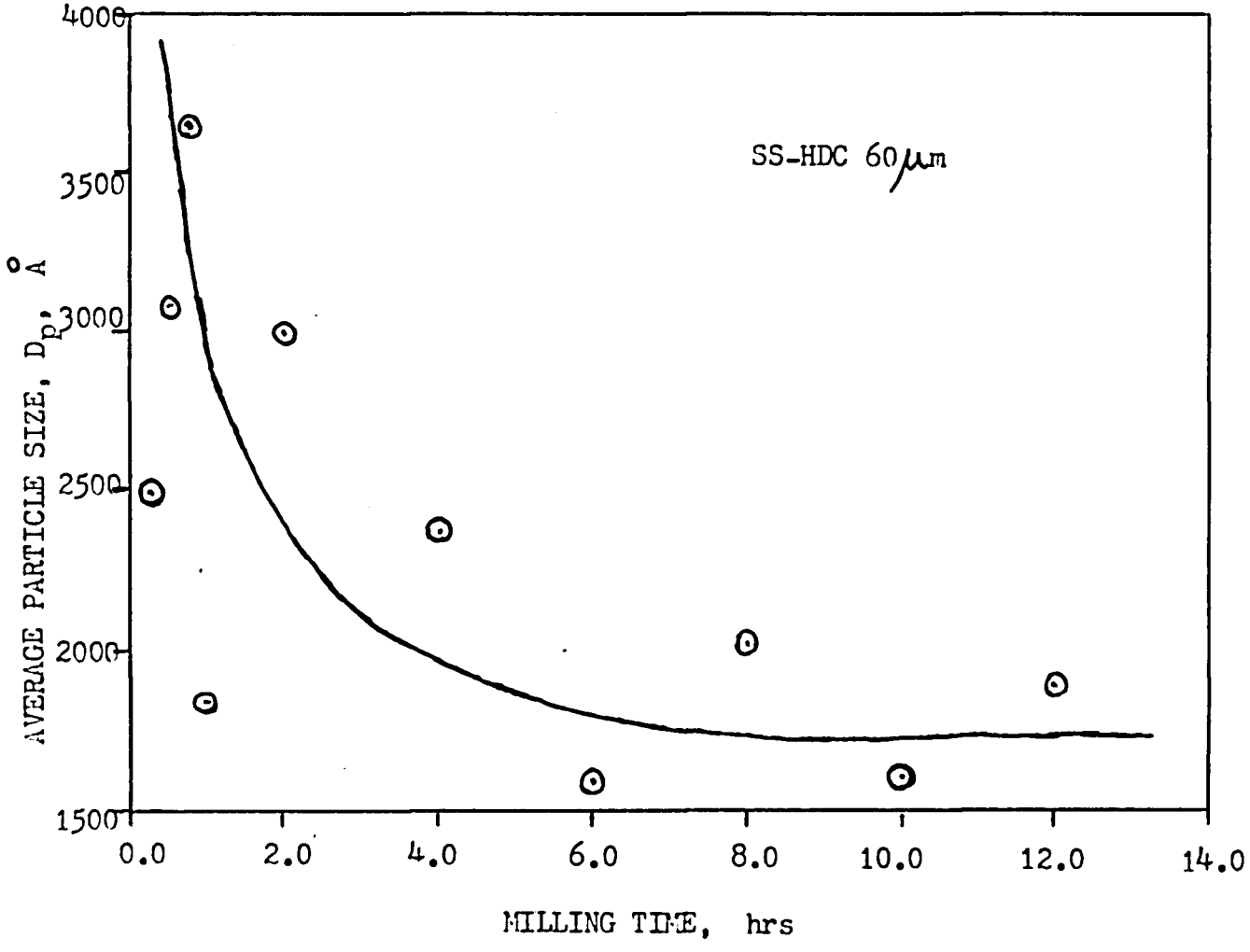



Figure 4.21 Effect of the milling time on the average particle size for the Diarylide Yellow pigment.

the average particle size as a function of the time of dispersion. As shown in Figure 4.21, the different points are scattered, indicating the lack of good separation between particles of closest size. Nevertheless, between the beginning and the end of the dispersion, the graph shows a visible decrease. The range of particle size is also very narrow, as in the HDC 20/μm.

Table 4.14

Differences in elution volume and average particle size (Diarylide Yellow)

| Time of dispersion | $\Delta V$ (ml) | $D_p$ (Å) |
|---|---|---|
| 15 min | 0.169 | 2483 |
| 30 min | 0.20 | 3081 |
| 45 min | 0.222 | 3641 |
| 1 h | 0.126 | 1839 |
| 2 h | 0.194 | 2981 |
| 4 h | 0.164 | 2361.5 |
| 6 h | 0.122 | 1608.5 |
| 8 h | 0.143 | 2032.5 |
| 10 h | 0.122 | 1608.5 |
| 12 h | 0.132 | 1901 |
| J67 sample | 0.04 | ~60 |

Similar to the two previous cases, the trend towards a more monodisperse dispersion is also observed, as shown in Figures 4.22 and 4.23 .

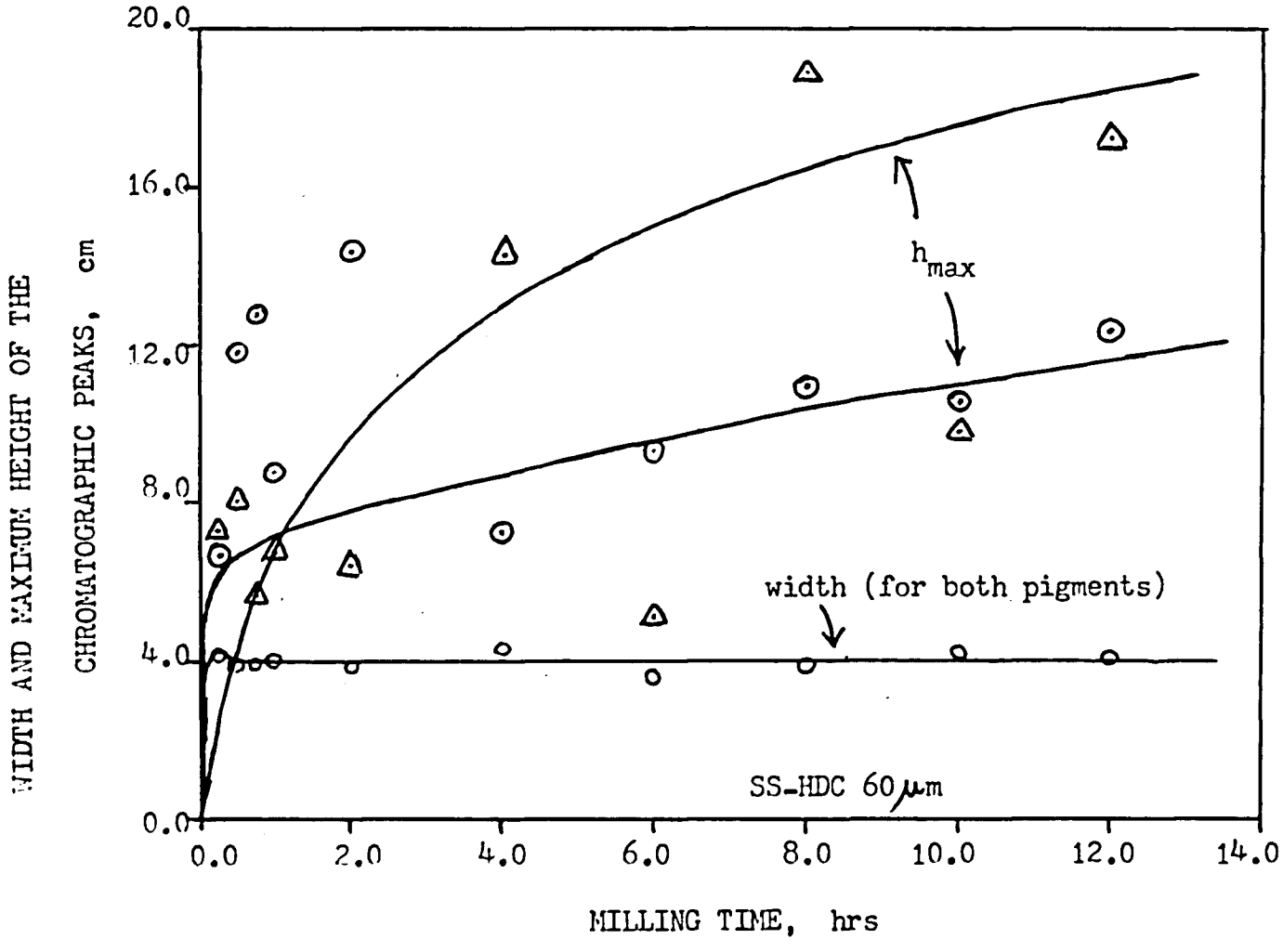



Figure 4.22 Effect of the milling time on the heights and widths of the peaks for both pigments (⊙ - Diarylide Yellow; △ - Medium Chrome Yellow).

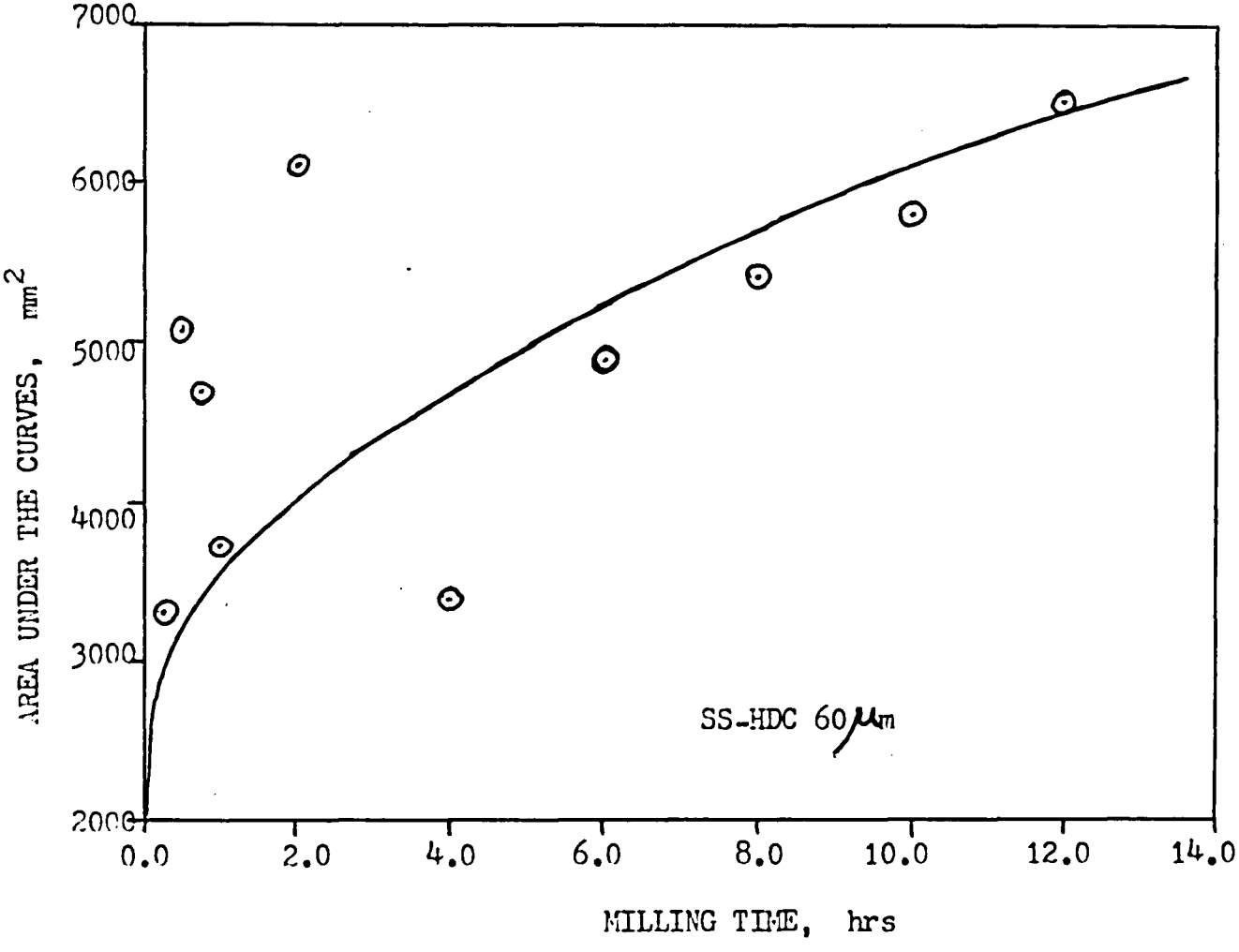



Figure 4.23 Effect of milling time on the areas under the peaks for the Diarylide Yellow pigment.

3. Results for the Medium Chrome Yellow pigment

The peaks are shown in Figure 4.24 for various times of dispersion, and, here, also, the vehicle solution is mixed with the pigment.

Table 4.15 shows the difference in elution volumes and the various average particle sizes with respect to the time of dispersion. With this rod-like shaped and larger-size pigment, the results obtained are difficult to interpret. The range of particle size is very narrow but there is, at least, a tendency for a decrease in size with the milling time, as shown in Figure 4.25 .

Table 4.15

Difference in elution volume and average particle size (Medium Chrome Yellow)

| Time of dispersion | $\Delta V$ (ml) | $D_p$ (Å) |
|---|---|---|
| 15 min | 0.164 | 2400 |
| 30 min | 0.09 | 840 (?) |
| 45 min | 0.185 | 2791 |
| 1 h | 0.157 | 2322 |
| 2 h | 0.154 | 2246 |
| 4 h | 0.195 | 2981 |
| 6 h | 0.147 | 2137 |
| 8 h | 0.258 | 4447 (?) |
| 10 h | 0.185 | 2791 |
| 12 h | 0.139 | 1998 |

Figure 4.22 and 4.26 show, again, an increase in peak height and peak area with the time of dispersion as shown in the chromatogram.

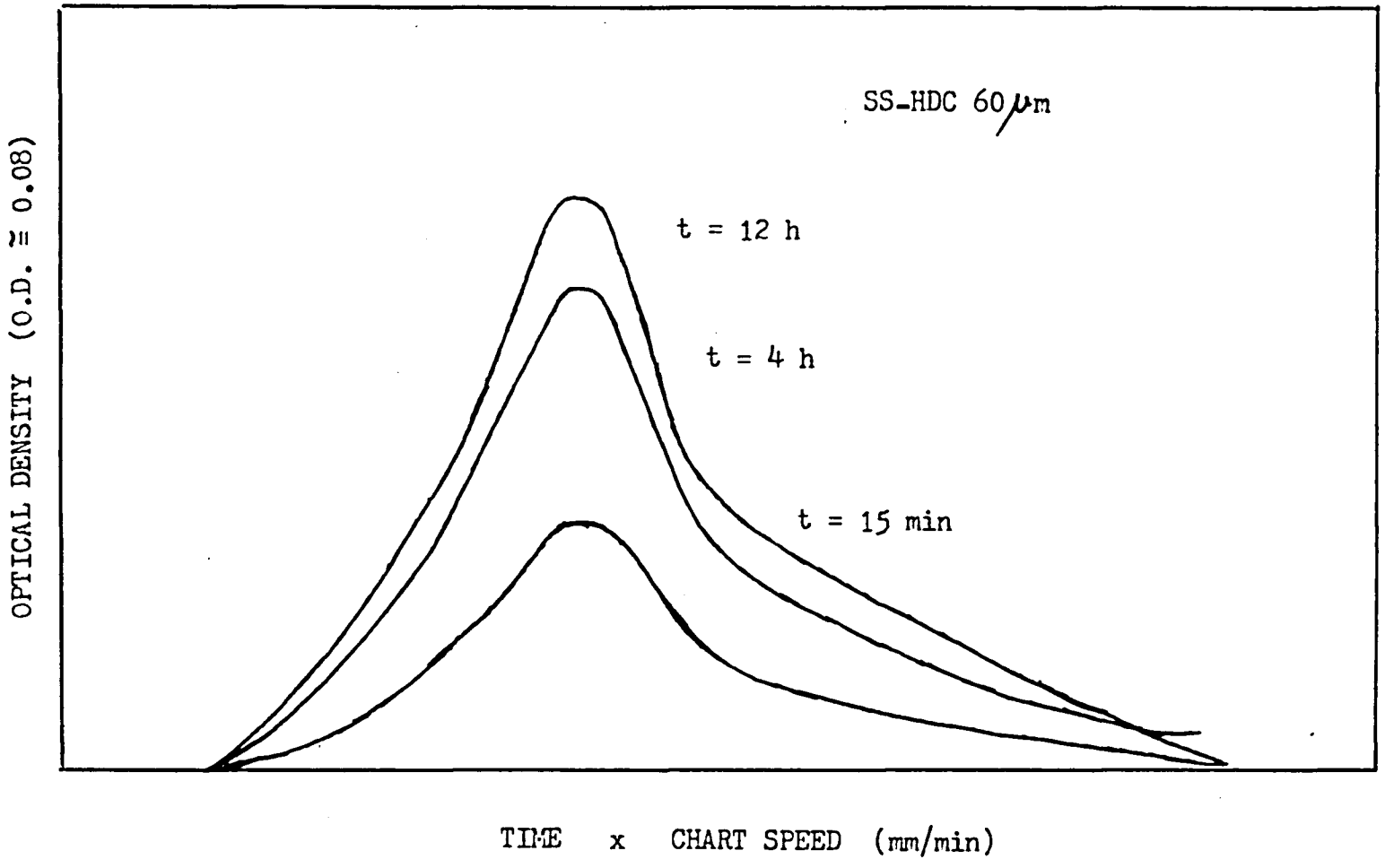



Figure 4.24 Chromatograms at various times of dispersion for the Medium Chrome Yellow pigment (chart speed = 25.4 mm/min).

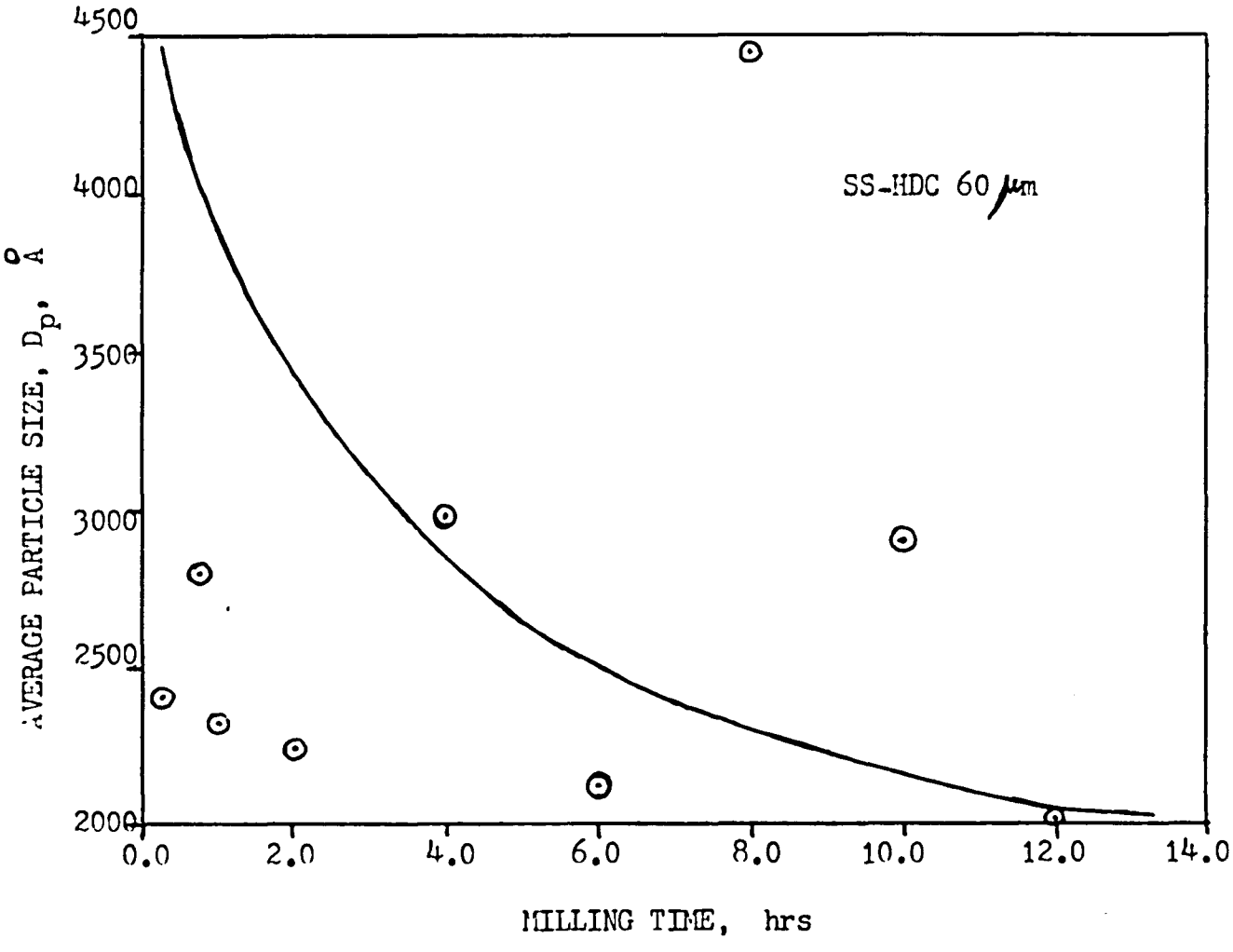



Figure 4.25 Effect of the milling time on the average particle size for the Medium Chrome Yellow pigment.

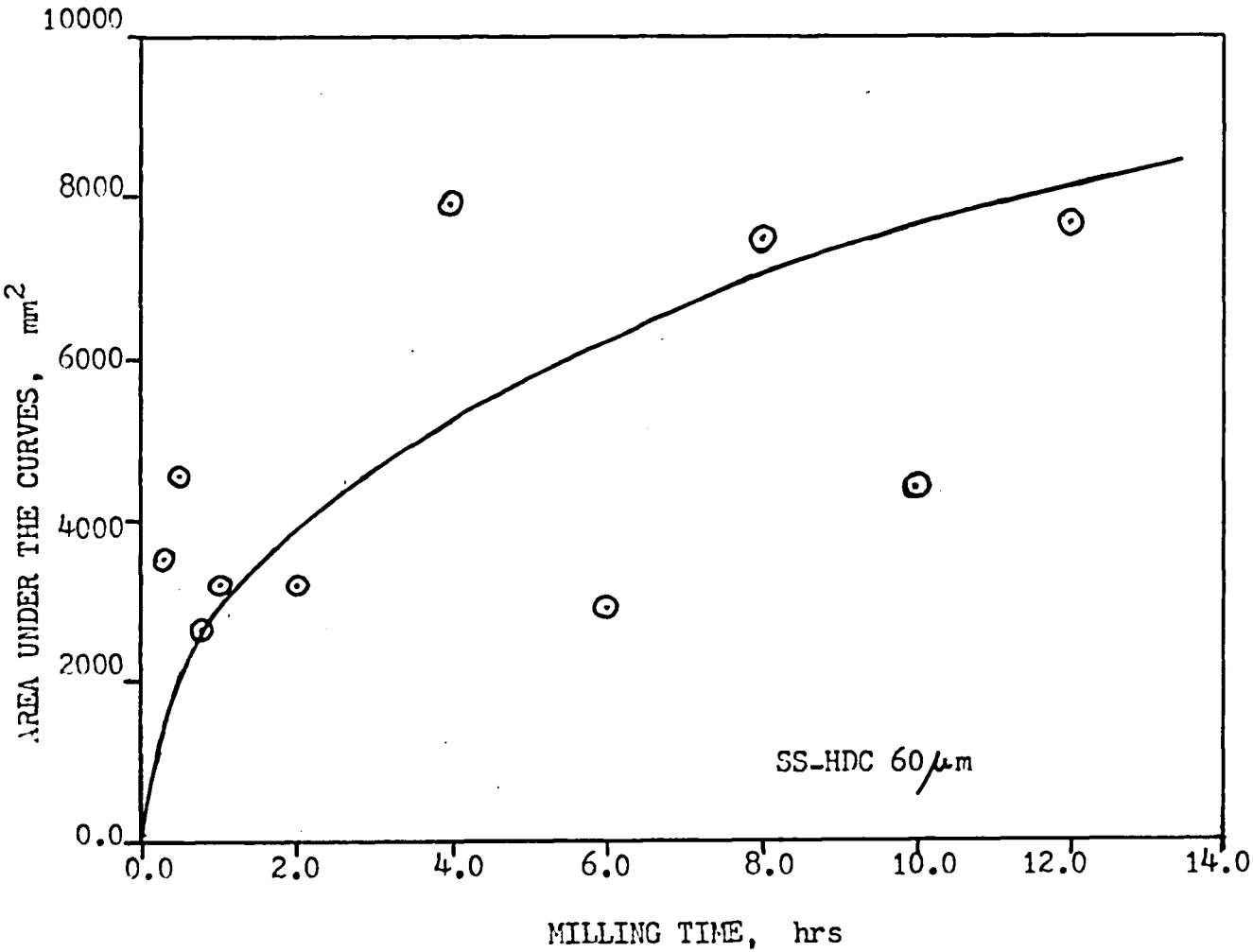



Figure 4.26 Effect of the milling time on the areas under the peaks for the Medium Chrome Yellow pigment.

VIII. Measurement of the pigment particle size by electron microscopy and color strength

1. Electron microscopy

a. Diarylide Yellow

Electron micrographs for different time of dispersion are shown in Figures 4.27 (a) to (d). The magnification is,in each case, (12,090X), which indicates that one centimeter corresponds to 8271 Å; and therefore, 1 micron = 1.21 cm. Table 4.16 shows the ink samples which are displayed.

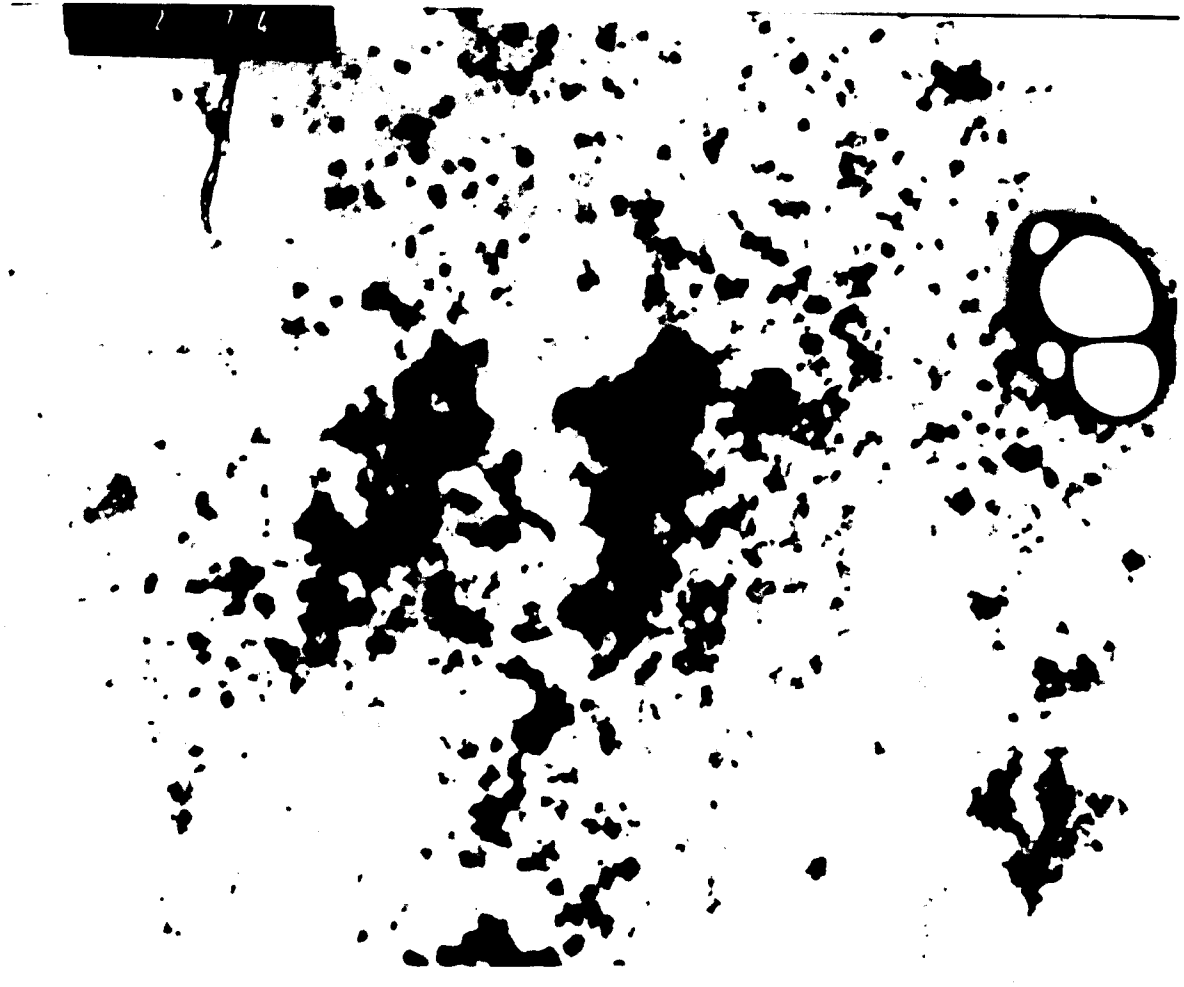
Table 4.16

Electron microscope pictures

| Picture's Number | Time of dispersion |
|---|---|
| 21746 | 15 min |
| 21741 | 2 h |
| 21743 | 4 h |
| 22847 | 12 h |

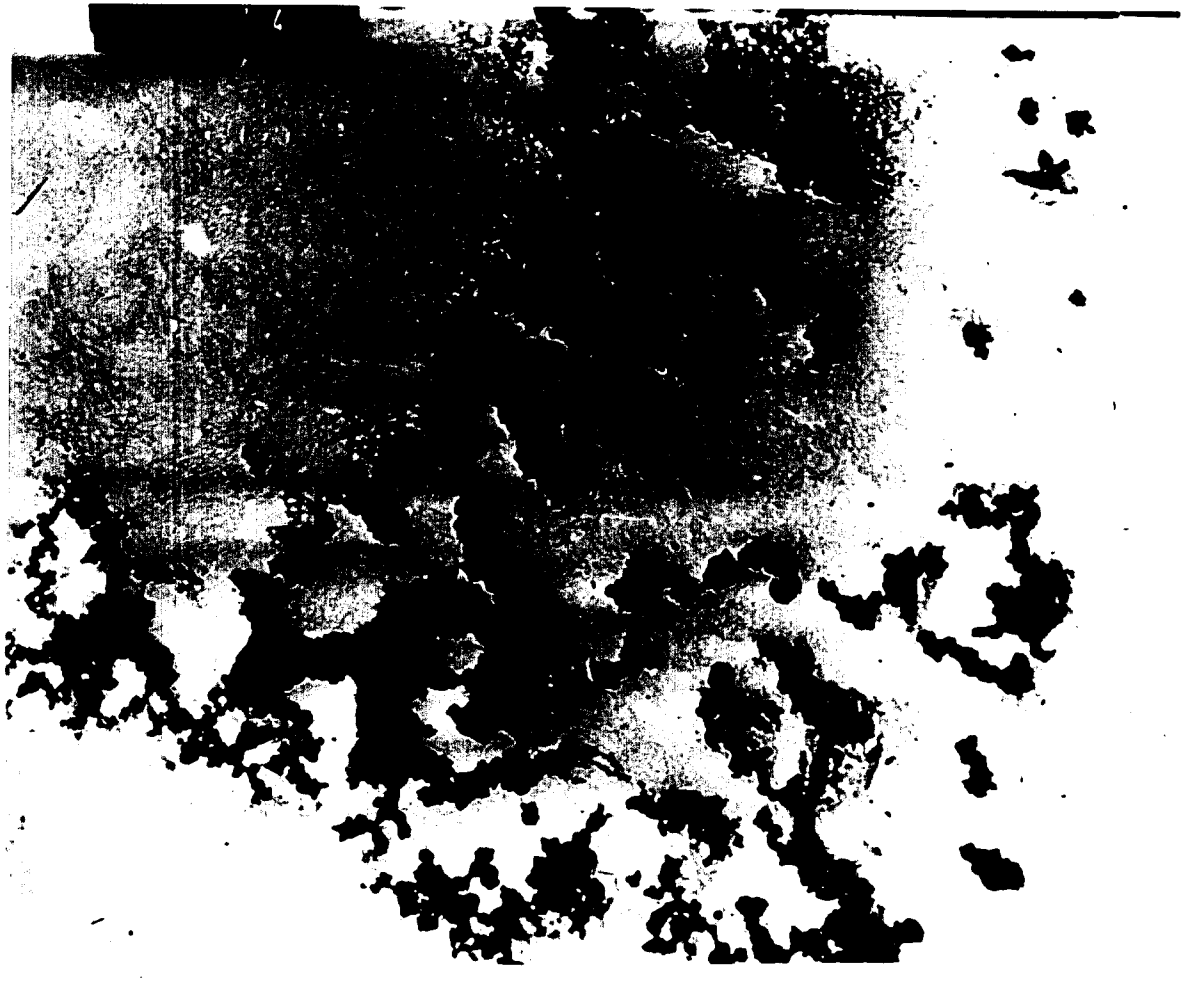
An optical micrograph was also taken, for a zero time of dispersion, and is shown in Figure 4.28 (Magnification : 500X). The average particle size reaches as much as 40 $\mu$m in diameter, and, therefore, can not be used for any chromatographic methods. The maximum allowed for tubular pinch is about 20 $\mu$m, but 10 $\mu$m is the usual limit.

Table 4.17 describes the effect of milling time on the average particle diameter. The magnification, in this case, was higher (21,060X); using bigger photographs permits more accurate measurements.



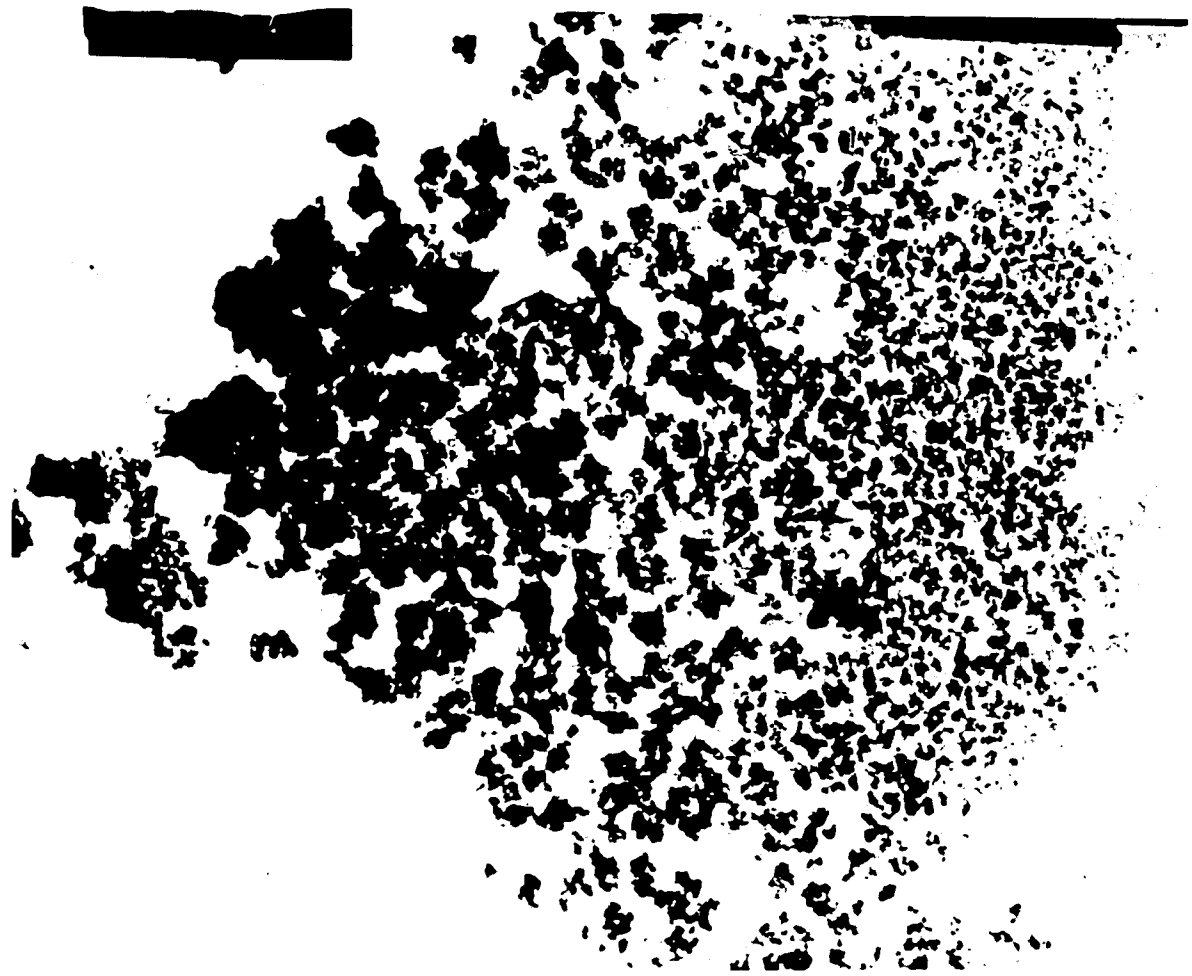
1μ

Figure 4.27 (a) Electron micrograph after 15 minutes of dispersion (pigment : Diarylide Yellow).



1 μ

Figure 4.27 (b) Electron micrograph after 2 hours dispersion (pigment : Diarylide Yellow).



$\leftarrow 1\mu \rightarrow$

Figure 4.27 (c) Electron micrograph after 4 hours of dispersion (pigment : Diarylide Yellow).

$\leftarrow 1\mu \rightarrow$

Figure 4.27 (d) Electron micrograph after 12 hours of dispersion (pigment : Diarylide Yellow).

Figure 4.28 Optical micrograph at zero time of dispersion for the Diarylide Yellow pigment. (Magnification : 500X) .



Figure 4.30 (a) Electron micrograph after 15 minutes of dispersion (pigment : Medium Chrome Yellow).



Figure 4.30 (b) Electron micrograph after 1 hour of dispersion (pigment : Medium Chrome Yellow).

Figure 4.30 (c) Electron micrograph after 4 hours of dispersion (pigment : Medium Chrome Yellow).

Figure 4.30 (d) Electron micrograph after 12 hours of dispersion (pigment : Medium Chrome Yellow).

Figure 4.31 Optical micrograph for zero dispersion in the case of Medium Chrome Yellow. (Magnification : 1600X)

these were made by using a Zeiss Integrator, for both ink batches. A curve is shown in Figure 4.29 .

Table 4.17

Electron microscope measurements
(Diarylide Yellow)

| Time of dispersion | Average diameter (mm) | | Average diameter (Å) | |
|---|---|---|---|---|
| | Batch #1 | Batch #2 | Batch #1 | Batch #2 |
| 15 min | 11.85 | 11.90 | 5626.5 | 6473 |
| 30 min | 12.60 | 10.90 | 5983 | 5929 |
| 45 min | 13.00 | 6.30 | 6173 | 3427 |
| 1 h | 8.20 | 10.00 | 3894 | 5440 |
| 2 h | 10.84 | 9.80 | 5150 | 5330 |
| 4 h | 8.70 | 9.40 | 4131 | 5113 |
| 6 h | 8.75 | 7.30 | 4155 | 3970 |
| 8 h | 7.45 | 5.80 | 3537 | 3155 |
| 10 h | 6.25 | 5.80 | 2968 | 3155 |
| 12 h | 6.00 | 4.50 | 2849 | 2448 |

b. Medium Chrome Yellow

The electron micrographs are shown in Figures 4.30 (a) to (d) (Magnification : 12,090X). Table 4.18 shows the different ink samples.

Again, an optical micrograph of a zero-time dispersion was taken, as shown in Figure 4.31 (Magnification : 1600X). The average particle size is about 30 $\mu$m.

Table 4.19 describes the average diameter as a function of the milling time with a magnification similar to that described for

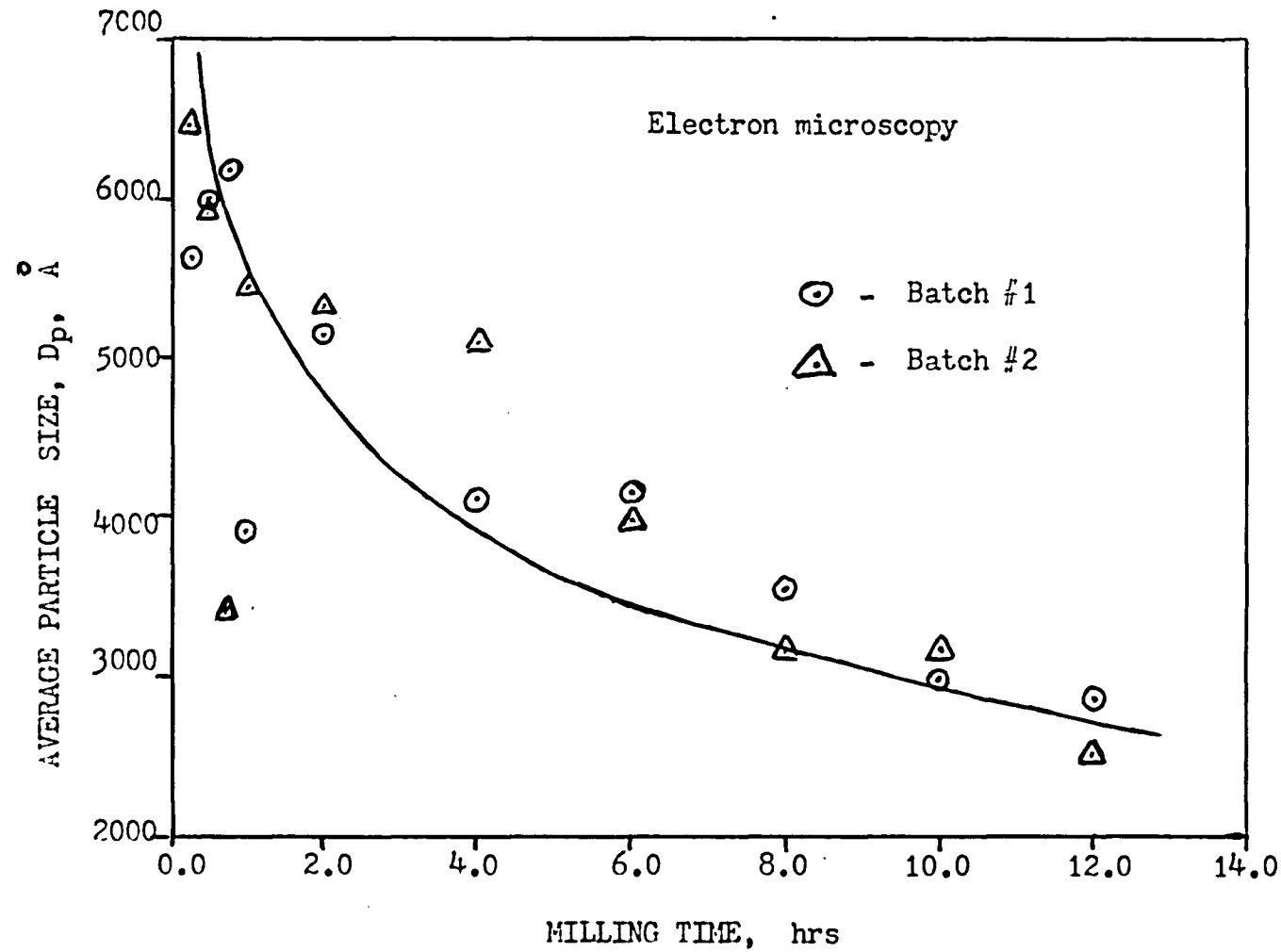



Figure 4.29 Effect of the milling time on the average particle size for the Diarylide Yellow pigment.

the previous case, i.e., 21,060X. Figure 4.32 shows the curve which was obtained from these results.

Table 4.18

Electron microscope pictures

| Picture's Number | Time of dispersion |
|---|---|
| 22665 | 15 min |
| 22668 | 1 h |
| 22670 | 4 h |
| 22674 | 12 h |

Table 4.19

Electron microscope measurements
(Medium Chrome Yellow)

| Time of dispersion | Average diameter (mm) | Average diameter (Å) |
|---|---|---|
| 15 min | 13.90 | 7560 |
| 30 min | 16.30 | 8866 |
| 45 min | 19.50 | 10600 |
| 1 h | 15.60 | 8485 |
| 2 h | 11.80 | 6418 |
| 4 h | 7.90 | 4297 |
| 6 h | 10.80 | 5874 |
| 8 h | 9.80 | 5330 |
| 10 h | 8.60 | 4678 |
| 12 h | 7.30 | 3971 |

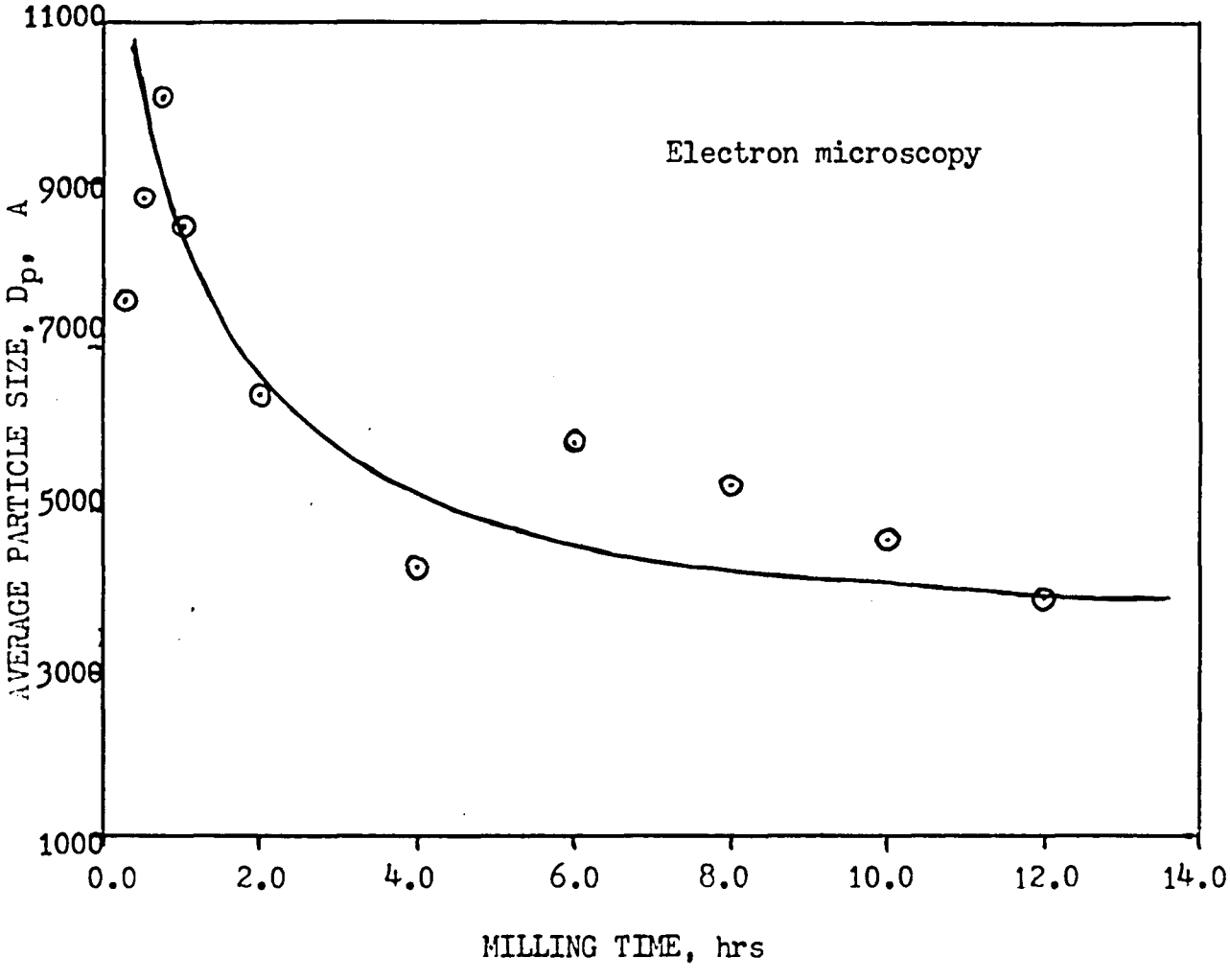



Figure 4.32 Effect of the milling time on the average particle size for the Medium Chrome Yellow pigment.

2. Color strength

As mentioned earlier in this chapter, some parallel work was carried out in this laboratory (4.1) using color strength as a method for measuring pigment dispersion. The ink formulation was identical, but only Diarylide Yellow was studied as a yellow pigment.

The experimental data are shown in Figure 4.33 . The reflectance values were taken at the wavelength of maximum absorption, i.e., 440, 560, and 610 nm for yellow, red, and blue, respectively.

When the experimental reflectance value, $R_m$, was converted into the K/S ratio, which was plotted against the colored pigment concentration, a curve which is concave downward is obtained instead of a straight line. This phenomenon results from the refractive index discontinuity between air and the film.

As can be seen from the graph, after 4 hours milling, a maximum is reached in the value of color strength for Diarylide Yellow. At this point, color strength has become independent of the particle size. This can be explained by the fact that, since the particle is very small at the maximum value of color strength, the substance within the particle has the same absorption effect as that in the surface regions, because the individual particle is still transparent. Therefore, even if, as shown in this work, we can have further reduction in size at longer time of dispersion, this can not yield additional absorption.

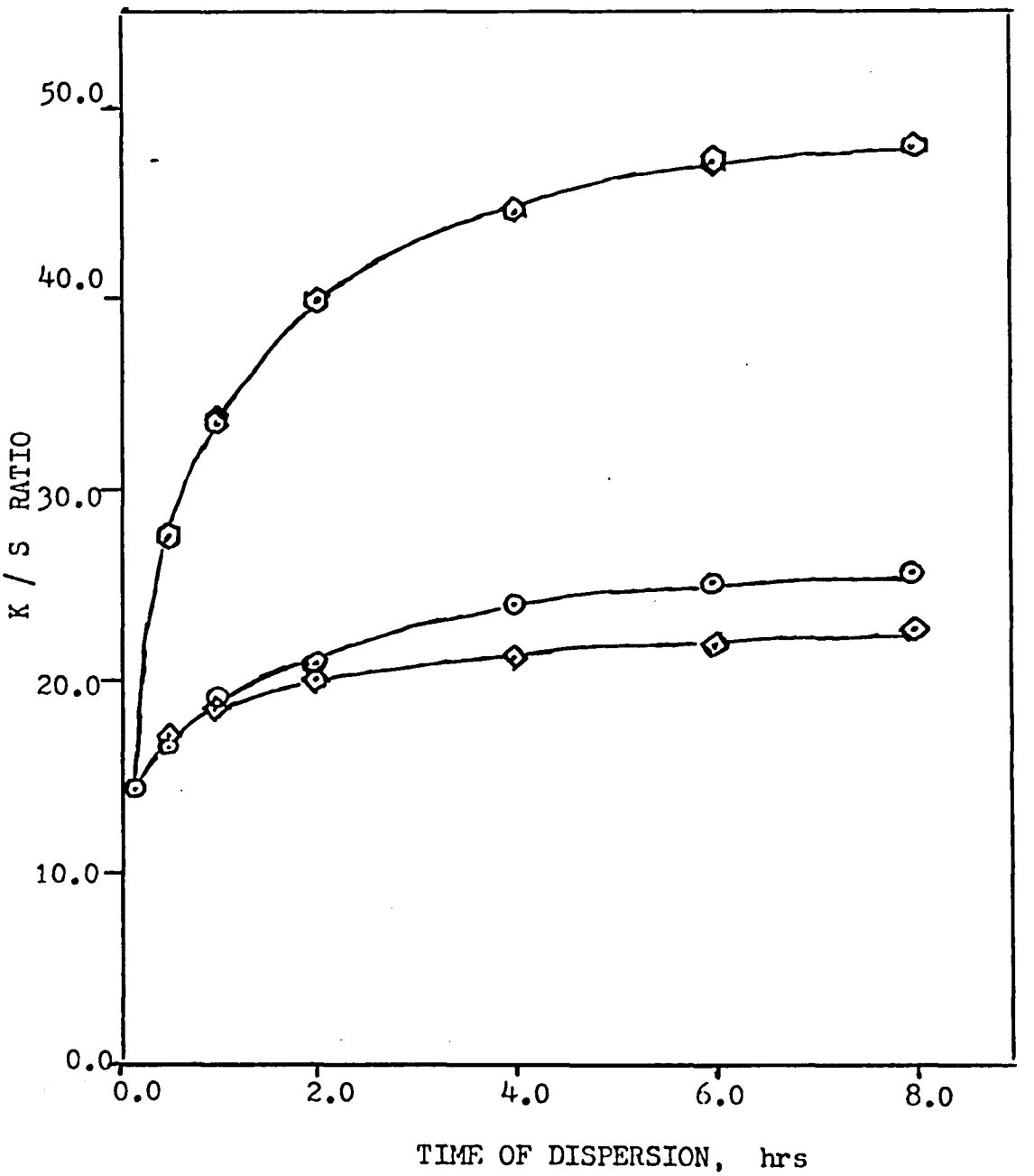



Figure 4.33 Color strength of Diarylide Yellow (⊙), Barium Lithol Red (◈), and Phtalocyanine Blue (⊙) in Joncryl 67 as a function of grinding time (4.1).

## IX. Discussion of the results obtained

### 1. Measurement of percent recovery

In a chromatogram, the y-axis is related to the turbidity deflection, $\tau$, while the x-axis corresponds to the time multiplied by the chart speed (mm/min).

The turbidity deflection corresponds to an 0.08 optical density, i.e., 10 5/16 inch or 794 mm. To measure a percentage recovery, the area in $mm^2$ must be changed in area (OD $cm^3$), as follows :

area ($mm^2$) (OD/mm) (1/chart speed) (flow rate) = area (OD $cm^3$)

$$\text{area (OD cm}^3\text{)} = \int \tau \, dV$$

$$\text{percent recovery} = \frac{\text{amount recorded}}{\text{amount injected}} = \frac{\left(c/\tau\right)^* \int \tau \, dV}{V_i \; C_i}$$

where $V_i$ = amount injected

$C_i$ = initial concentration of injected sample

$\left(c/\tau\right)^*$ = inverse of slope in a plot of O.D. versus % total solid content

The $\left(c/\tau\right)^*$, usually, varies with particle size of monodisperse polystyrene latex, and so, can not be used in our polydisperse pigmented system.

In our case, since tubular pinch chromatography provides almost 100% recovery, the different values of the areas in (OD $cm^3$) were computed, as a function of the grinding time, and the results obtained from the two other chromatographic methods were compared, knowing the different flow rates, optical density, and chart speed.

Table 4.20 compares the percent recovery for the Diarylide

Table 4.20

Percent recovery (Diarylide Yellow)

| Time of dispersion | Tubular pinch area ($mm^2$) | Tubular pinch area ($ODcm^3$) | SS-HDC 60 μm area ($mm^2$) | SS-HDC 60 μm area ($ODcm^3$) | HDC 20 μm area ($mm^2$) | HDC 20 μm area ($ODcm^3$) | SS-HDC 60 μm % recovery | HDC 20 μm % recovery |
|---|---|---|---|---|---|---|---|---|
| 15 min | 8924 | 0.085 | 3287 | 0.0278 | 7254 | 0.025 | 32.7 | 29.4 |
| 30 min | 11605 | 0.110 | 5076 | 0.086 | 6413 | 0.0433 | 78.2 | 39.4 |
| 45 min | 11311 | 0.108 | 4690 | 0.079 | 5592 | 0.038 | 73.0 | 35.2 |
| 1 h | 9646 | 0.092 | 3731 | 0.016 | 5439 | 0.037 | 17.4 | 40.2 |
| 2 h | 10912 | 0.104 | 6115 | 0.103 | 7224 | 0.049 | 99.0 | 47.0 |
| 4 h | 11583 | 0.110 | 3378 | 0.029 | 9625 | 0.065 | 26.4 | 59.1 |
| 6 h | 11512 | 0.1096 | 4900 | 0.021 | 9560 | 0.065 | 19.2 | 59.3 |
| 8 h | 11950 | 0.114 | 5428 | 0.023 | 9549 | 0.065 | 20.2 | 57.0 |
| 10 h | 14055 | 0.134 | 5831 | 0.025 | 10975 | 0.074 | 18.7 | 55.2 |
| 12 h | 10492 | 0.100 | 6523 | 0.028 | - | - | 28.0 | - |

Table 4.21

Percent recovery (Medium Chrome Yellow)

| Time of dispersion | Tubular pinch area ($mm^2$) | Tubular pinch area ($ODcm^3$) | SS-HDC 60 $\mu m$ area ($mm^2$) | SS-HDC 60 $\mu m$ area ($ODcm^3$) | SS-HDC 60 $\mu m$ % recovery |
|---|---|---|---|---|---|
| 15 min | 11168 | 0.0266 | 3563 | 0.00753 | 28.3 |
| 30 min | 13805 | 0.033 | 4560 | 0.00964 | 29.2 |
| 45 min | 12391 | 0.0295 | 2635 | 0.00557 | 18.9 |
| 1 h | 12604 | 0.030 | 3193 | 0.00675 | 22.5 |
| 2 h | 12668 | 0.030 | 3196 | 0.00676 | 22.52 |
| 4 h | 15483 | 0.037 | 7924 | 0.0168 | 45.4 |
| 6 h | 15367 | 0.0366 | 2409 | 0.00509 | 13.9 |
| 8 h | 16219 | 0.0386 | 7502 | 0.0159 | 41.2 |
| 10 h | 14834 | 0.0353 | 4371 | 0.00924 | 26.2 |
| 12 h | 15653 | 0.0373 | 7707 | 0.0163 | 43.7 |

Yellow pigment, and Table 4.21 for the Medium Chrome Yellow.

As we can see from thses tables, the SS-HDC 60$\mu$m gives a higher percent recovery at higher particle size and then at lower time of dispersion while it is the reverse for the HDC 20$\mu$m. Nevertheless, compared to the tubular pinch chromatography, they are both far behind and, therefore, will not give us accurate and reliable results we need for these polydisperse systems.

2. Comparison with the electron microscopy

Table 4.22 compares the respective average particle sizes for the three chromatographic methods compared to the results obtained for the electron microscope. As an example, the Diarylide Yellow, batch #1, will be chosen.

From these results, it is, then, obvious that the tubular pinch chromatography presents the more reliable chromatographic method for measuring the average particle size of pigments in water-based flexographic inks. It is, besides, quick, reproducible and easy to handle, and, usually, almost 100% of the samples are recovered, within experimental error.

We have also shown that this method can be applied for both organic and inorganic yellow pigments, independently of their shape, something which can enhance the power of this method.

Table 4.22

Comparison between chromatographic methods and electron microscope (Diarylide Yellow, batch #1)

| Time of dispersion | Tubular pinch | SS-HDC 60 μm | HDC 20 μm | Electron microscopy |
|---|---|---|---|---|
| 15 min | 6003 | 2483 | 2441 | 5626.5 |
| 30 min | 5340 | 3081 | 2566 | 5983 |
| 45 min | 5599 | 3641 | 2697 | 6173 |
| 1 h | 5170 | 1839 | 2566 | 3894 |
| 2 h | 4999.5 | 2981 | 2208.5 | 5150 |
| 4 h | 4372 | 2361.5 | 2210 | 4131 |
| 6 h | 3993.5 | 1608.5 | 2566 | 4155 |
| 8 h | 3191.5 | 2032.5 | 2441 | 3537 |
| 10 h | 2467 | 1608.5 | 2100 | 2968 |
| 12 h | 2308.5 | 1901 | - | 2849 |

## X. References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## Chapter 5

### Conclusion and Recommendations for further studies

If we refer back to the chapter 1, we have available some criteria by which a new technique for determining the particle size of pigments can be judged.

The tubular pinch chromatography we described and presented in the previous chapters as a new promising method can be criticized and commented on the basis of these criteria, i.e., sensitivity, versatility and applicability.

The first criterion, sensitivity, is related to the suitability of a technique in the sub-micron size range, a field for most pigmented systems. This chromatographic method offer the best separation for particles, usually, above 8000 Å or 0.8 µm; nevertheless, reasonable resolutions can be obtained even for particles as low as 2000 Å, as long as we compare particles of relatively different sizes. As a result, if we compare times of dispersion of 8 hours and 10 hours, we won't have as strong a separation as if times of 1 hour and 10 hours were compared.

The second criterion, versatility, depends on the wide variety of pigments and vehicles which are encountered in practice. Since this approach is new, only one type of colored pigment and one type of vehicle were used. But, at least, this method was shown to be reliable for both organic and inorganic pigment, with completely different shape. The scope of this work was also restricted to aqueous liquid inks, since these chromatographic methods had been used and studied mainly for polymer latexes.

The third criterion, applicability, is related to the colloidal nature of pigment dispersion. If the system has to be diluted for the purpose of the experiment, as it was in this work, there is a possibility of dilution shock which can occur. This drawback can be avoided by gradually diluting the ink samples, and it has been found in our case, that the sodium lauryl sulfate eluting solution used as a diluting media stabilizes fairly well our pigmented systems, even after as long as eight months; whereas only water as a diluent creates, after two months, a complete breakdown of the dispersion.

On the other hand, the fact that we need very low concentration of pigments before injection through these chromatographic systems doesn't present perfect insurance the results we get correspond really to what we have in our concentrated ink samples.

As a conclusion, compared to most of the methods used for assessing pigment dispersion, this tubular pinch chromatographic method represents an interesting and promising tool, especially for quality control laboratories. It is quick and reproducible, and, contrary to the grind gauge, it gives accurate numbers and values for the average particle size of pigments as a function of the grinding time. Compared to the electron microscope, the results are relatively similar,for a cost, which, in the case of tubular pinch chromatography, is greatly reduced.

Obviously, there is still much research to be carried out to understand the theoretical aspects of this chromatographic method. A model could be proposed in order to get, instead only of an average

particle size, rather a particle size distribution, based on theoretical results found and applied for hydrodynamic chromatography.

Then, the scope of applications could be broadened, using and studying other kind of pigments, vehicles, even non-aqueous media.

The separation, in this method, even at lower particle size, could also be improved, if the diameter of the stainless-steel capillary coil could be reduced --it is presently of the order of 200 $\mu$m--; the sensitivity of the method would, then, be widely improved.

## Appendix

## Glass-Column Packing and Cleaning Procedure for HDC Styrene-Divinylbenzene Copolymer Bead Packing

### A. Column Packing Procedure for HDC Packing

The empty glass column is set up for packing in the following manner. The outlet plunger assembly is connected to the bottom of the glass tube, along with a 40$\mu$m filter cloth screen. The column is placed in a vertical position, and water is added to be sure it can drip freely through the outlet plunger assembly. A one percent solution of SLS is prepared and then added to fill the empty column, and the bottom outlet tube of the plunger assembly is capped. A small amount of Dowex 50 cation exchange resin (75-100$\mu$m) is added to the SLS solution in the column and allowed to settle to the bottom until it forms a layer of approximately 2 to 3 mm over the 40$\mu$m filter screen of the plunger assembly.

The cleaned styrene-divinylbenzene copolymer bead packing is prepared as a 50% slurry in the SLS solution and thoroughly agitated to insure no particle agglomeration. With a 250 ml funnel attached to the top of the column, the packing slurry is slowly poured into the SLS solution of the column. The packing will quickly settle to the bottom of the tube on top of the ion exchange resin. Care must be taken to be sure the column fills evenly with packing. Add the entire amount of slurry to the funnel, and allow it to settle into the column. For best results, the column should be filled in one " shot ". In other words, layering of the packing into the column should be avoided. To help the settling process, uncap the bottom

outline from the plunger assembly and allow the SLS to drip through the column (this will eventually cease as the packing settles and fills the column). The settling process normally takes about 24 hours.

Once the packing has firmly settled and filled to the top of the column, remove the funnel and scrape out just enough packing to leave room for the inlet plunger assembly. With a 40 $\mu$m filter screen on the plunger assembly, carefully push tha assembly into the column until it rests firmly on top of the packed bed. Tighten all fittings and begin to pump the eluant through the column. Normally, several hours will be needed to remove all the one percent SLS solution from the column.

If the column packing has properly settled, virtually no compression of the packing should occur under a pressure of several hundred psi. If significant compression occurs ($>$1 cm), then the column may have to be repacked or allowed to settle for a longer period of time. Over a long period of continued use, some compression of the packing may occur, such as a couple of mm, and the inlet plunger assembly should be pushed down to rest snugly on top of the bed. Any void space between the plunger assembly and the top of the packing bed should be avoided.

The direction of eluant flow through the column should never be altered. The direction of flow should be maintained in the same manner as the column was packed --outlet side with the ion-exchange resin, inlet plunger resting firmly at the top of the packed bed. Over a period of time, it may be necessary to remove the plunger to change the filter screens. The same direction of flow must still be

maintained afterward. Never allow the packing material to go dry. Cap the column at both ends if not in use.

B. Cleaning of the HDC Styrene-Divinylbenzene Bead Packing

The following procedure, as recommended by H. Small, should be employed for cleaning the HDC packing. The packing should be cleaned in bulk, with the aid of a one- or two-liter Büchner, fritted glass ($< 15 \mu m$) filtering funnel and two-liter filtering flask. The sequence of steps is as follows :

1. Place the aqueous packing slurry in the Büchner funnel,
2. Wash with 2 liters of 1% SLS,
3. Distilled water, 2 liters,
4. Hot, 3N NaOH (70-80 °C), 2 liters,
5. Hot, distilled water, 2 liters,
6. Distilled water, 2 liters,
7. Hot, 3N HCl (70-80 °C), 2 liters,
8. Hot, distilled water, 2 liters,
9. Distilled water, 2 liters,
10. Hot, methanol, boiling, 2 liters,
11. Distilled water, 4 liters,
12. 1% SLS, 2 liters, and store for packing.

# VITA

Philippe Huwart was born on July 19, 1953, in Herentals, Belgium, the son of Georgette and Jean-Jacques Huwart. After attending High School, section Latin-Greek in Brussels, he followed a Master in Chemistry at the University of Louvain-La-Neuve and graduated in 1975. The year after, he received a Degree in Business Administration at the same University. In September 1977, he started working at his father printing ink manufactory, S.P.R.L. Martin-Huwart, in Vilvoorde, Belgium, as a research chemist. In August, 1978 , he entered the Graduate School at Lehigh University.